Klug, H. P. (1966). *Acta Cryst.* **21**, 536–546.

Mazid, M. A., Razi, M. T. & Sadler, P. J. (1981). *Inorg. Chem.* **20**, 2872–2877.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Stephens, J. (1973). *MOLGEOM*. Adapted from *CUDLS*. McMaster Univ., Hamilton, Canada.

Stewart, J. M. & Hall, S. R. (1983). *The XTAL System of Crystallographic Programs*. Tech. Rep. TR-1364. Univ. of Maryland, College Park, MD 20742, USA.

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Structure of *rac*-Bromo(1,4,7,11,14-pentaazacycloheptadecane)cobalt(III) Tetrabromozincate(II)

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Abstract. $[CoBr(C_{12}H_{29}N_5)][ZnBr_4]$, $M_r = 767{\cdot}25$, monoclinic, $P2_1/n$, $a = 8{\cdot}399\,(2)$, $b = 18{\cdot}784\,(3)$, $c = 14{\cdot}688\,(3)$ Å, $\beta = 103{\cdot}12\,(2)°$, $V = 2256{\cdot}7\,(14)$ Å^3, $Z = 4$, $D_x = 2{\cdot}26$, $D_m = 2{\cdot}250$ g cm^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 106$ cm^{-1}, $F(000) = 1472$, room temperature, $R = 0{\cdot}033$ for 3189 reflections. The structure consists of an octahedral cobalt(III) cation with five nitrogens of the macrocycle and a Br^- ion in the coordination sphere and an unexceptional tetrahedral tetrabromozincate anion. The macrocycle is coordinated to the Co^{III} with the 6,5,6 arrangement of chelate rings in the plane of the four N atoms and the configuration of the chiral N centres is 1*RS*, 7*SR*, 11*RS*, 14*RS*.

Introduction. Isolation and characterization of cobalt(III) complexes of a series of pentaazamacrocyclic ligands has been described (Curtis, Osvath & Weatherburn, 1987). The ligand 1,4,7,11,14-pentaazacycloheptadecane is unusual in that two isomeric forms can be isolated. The α-isomer was identified by ^{13}C NMR as one of two possible *meso* isomers of the form of the complex with the 6,5,6 arrangement of chelate rings in the plane of the four N atoms (Hay, Bembi, McLaren & Moodie, 1984; Bombieri, Forsellini, Del Pra, Cooksey, Humanes & Tobe, 1982). The other isomer isolated could not be identified on the basis of its ^{13}C NMR spectrum so a crystal structure analysis was undertaken. The complex has the same arrangement of the macrocyclic ligand about the Co as the α-isomer but is the racemate.

Table 1. *Positional parameters and their e.s.d.'s*

	x	y	z	B_{eq}(Å^2)
Br(1)	−0·11164 (7)	0·05330 (3)	0·61745 (4)	3·65 (1)
Br(2)	0·06483 (7)	0·27052 (3)	1·10292 (4)	3·02 (1)
Br(3)	−0·24131 (7)	0·10708 (3)	1·07073 (4)	3·24 (1)
Br(4)	−0·05811 (8)	0·18181 (3)	1·31853 (4)	3·66 (1)
Br(5)	0·22479 (7)	0·07796 (3)	1·17852 (5)	3·99 (1)
Zn	0·00281 (8)	0·15851 (3)	1·16872 (5)	2·86 (1)
Co	0·10484 (8)	0·11254 (3)	0·72495 (5)	2·09 (1)
N(1)	0·2469 (5)	0·0246 (2)	0·7418 (3)	3·2 (1)
N(2)	0·1995 (5)	0·1491 (2)	0·6203 (3)	2·75 (9)
N(3)	−0·0267 (5)	0·2014 (2)	0·7072 (3)	2·49 (9)
N(4)	0·0027 (5)	0·0828 (2)	0·8270 (3)	2·50 (9)
N(5)	0·2796 (5)	0·1540 (2)	0·8240 (3)	2·30 (9)
C(1)	0·2775 (7)	−0·0098 (3)	0·6545 (5)	4·2 (1)
C(2)	0·3527 (7)	0·0406 (3)	0·5953 (4)	4·3 (1)
C(3)	0·2388 (7)	0·0986 (3)	0·5501 (4)	3·8 (1)
C(4)	0·0890 (7)	0·2060 (3)	0·5716 (4)	3·3 (1)
C(5)	0·0388 (7)	0·2501 (3)	0·6447 (4)	3·2 (1)
C(6)	−0·0550 (7)	0·2416 (3)	0·7897 (4)	3·2 (1)
C(7)	−0·1421 (6)	0·1971 (3)	0·8504 (4)	3·0 (1)
C(8)	−0·1565 (6)	0·1184 (3)	0·8283 (4)	2·9 (1)
C(9)	0·1215 (6)	0·0864 (3)	0·9186 (4)	3·0 (1)
C(10)	0·2386 (7)	0·1473 (3)	0·9180 (4)	2·9 (1)
C(11)	0·4344 (6)	0·1175 (3)	0·8201 (4)	3·2 (1)
C(12)	0·4039 (7)	0·0389 (3)	0·8127 (4)	3·7 (1)

The equivalent isotropic displacement parameter B_{eq} is: $\frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Experimental. Preparation of the complex as reported (Curtis, Osvath & Weatherburn, 1987). Triangular prismatic crystals, 0·35 × 0·17 × 0·15 mm, density by flotation in CH_2Br_2/CCl_4; preliminary examination and data collection performed on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Accurate unit-cell dimensions and an orientation matrix by least-squares fit of diffracting positions of 25 reflections ($21 \le 2\theta \le 27°$). Data collected using the $\theta/2\theta$ technique to a maximum 2θ of 54·9°, ω scan ranges $(0{\cdot}6 + 0{\cdot}35\tan\theta)°$. Gradual decrease in intensities of four representative reflections monitored every 60 min of X-ray exposure. Loss of intensity reached

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10·1% over 101·2 h (max. correction factor 1·05, average 1·02). Correction for Lorentz, polarization and crystal decay. Both empirical and numerical absorption corrections applied and the resulting data were averaged. 11 014 reflections measured, 5136 were unique and not systematically absent. Equivalent reflections were averaged (R_{merge} 2·9%). Structure solved using direct methods. All hydrogens were located, added to structure factor calculations at calculated positions but not refined. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$, where w, the weight, $= \{[\sigma_2(F_o)]^{-1}\}$, converged (max. $\Delta/\sigma = 0{\cdot}05$) to $R = 0{\cdot}033$ and $wR = 0{\cdot}034$ for 3189 observed data with $I > 2\sigma(I)$; max. and min. peaks of final ΔF synthesis 0·51 e Å^{-3} at 1·7 Å from Br(5) and −0·95 e Å^{-3} at 0·8 Å from Br(5). Programs *SDP/VAX* (Frenz, 1978) on a VAX-11/730 computer. Atomic scattering factors from Cromer & Waber (1974), anomalous-dispersion effects in F_c (Ibers & Hamilton, 1964) and f' and f'' from Cromer (1974).

Discussion. Atomic positional parameters and their e.s.d.'s are given in Table 1.* A view of the complex cation showing the atom-numbering scheme is given in Fig. 1, while important bond distances and bond angles are given in Table 2. The structure contains discrete ions at general positions in the unit cell (Fig. 2). There are six interionic contact distances less than 3·65 Å between bromines of the $ZnBr_4^{2-}$ anion and the light atoms of the cation. Four of these involve an N atom on the macrocycle and are indicative of hydrogen-bonding interactions; Br(2)—N(2) 3·48, Br(2)—N(3) 3·47, Br(4)—N(4) 3·57 and Br(4)—N(5) 3·38 Å. The angles are Br(2)—HN(2)—N(2) 138, Br(2)—HN(3)—N(3) 142, Br(4)—HN(4)—N(4) 153, Br(4)—HN(5)—N(5) 156°. The other short contacts are between C(3) and Br(2) (3·63 Å) and C(5) and Br(3) (3·56 Å). There is one short cation–cation contact between C(8) and C(11) (3·41 Å). The molecular structure of the anion is unexceptional. The cation consists of a central Co ion in a nearly octahedral environment provided by one Br ion and the macrocyclic ligand. The Co—Br distance is normal and similar to that in the related 19-membered pentaaza-macrocyclic complex (2·386 Å). The Co—N distances are also in the range found for other pentaazamacrocyclic complex (2·386 Å). The Co—N bieri *et al.*, 1982; Curtis, Gainsford, Osvath & Weatherburn, 1987). The macrocycle is coordinated with both six-membered chelate rings in the equatorial plane of four N atoms. The formal configurations of the coordinated chiral secondary amine centres are

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Zn—Br(2)	2·4211 (9)	Zn—Br(3)	2·4236 (9)
Zn—Br(4)	2·4096 (9)	Zn—Br(5)	2·3803 (9)
Co—Br(1)	2·3955 (9)	Co—N(1)	2·020 (5)
Co—N(2)	2·006 (5)	Co—N(3)	1·986 (4)
Co—N(4)	1·969 (4)	Co—N(5)	1·977 (4)
N(1)—C(1)	1·509 (8)	N(1)—C(12)	1·508 (4)
N(2)—C(3)	1·492 (7)	N(2)—C(4)	1·488 (8)
N(3)—C(5)	1·487 (8)	N(3)—C(6)	1·494 (7)
N(4)—C(8)	1·499 (7)	N(4)—C(9)	1·485 (7)
N(5)—C(10)	1·503 (7)	N(5)—C(11)	1·483 (7)
C(1)—C(2)	1·517 (9)	C(2)—C(3)	1·50 (1)
C(4)—C(5)	1·490 (9)	C(6)—C(7)	1·524 (8)
C(7)—C(8)	1·514 (8)	C(6)—C(7)	1·524 (8)
C(11)—C(12)	1·499 (8)	C(9)—C(10)	1·510 (8)

Br(2)—Zn—Br(3)	109·82 (3)	Br(2)—Zn—Br(4)	108·43 (3)
Br(2)—Zn—Br(5)	109·89 (3)	Br(3)—Zn—Br(4)	106·78 (3)
Br(3)—Zn—Br(5)	109·16 (3)	Br(4)—Zn—Br(5)	112·69 (4)
Br(1)—Co—N(1)	92·3 (2)	Br(1)—Co—N(2)	91·6 (1)
Br(1)—Co—N(3)	89·3 (1)	Br(1)—Co—N(4)	88·5 (1)
Br(1)—Co—N(5)	173·8 (1)	N(1)—Co—N(2)	92·8 (2)
N(1)—Co—N(3)	117·5 (2)	N(1)—Co—N(4)	91·3 (2)
N(1)—Co—N(5)	85·0 (2)	N(2)—Co—N(3)	85·2 (2)
N(2)—Co—N(4)	176·0 (2)	N(2)—Co—N(5)	94·1 (2)
N(3)—Co—N(4)	90·7 (2)	N(3)—Co—N(5)	93·7 (2)
N(4)—Co—N(5)	86·1 (2)	C(1)—N(1)—C(12)	111·8 (2)
C(3)—N(2)—C(4)	109·7 (5)	C(5)—N(3)—C(6)	109·8 (4)
C(8)—N(4)—C(9)	112·8 (4)	C(10)—N(5)—C(11)	112·4 (4)
N(1)—C(1)—C(2)	113·2 (5)	C(1)—C(2)—C(3)	113·6 (4)
N(2)—C(3)—C(3)	112·0 (5)	N(2)—C(4)—C(5)	107·6 (5)
N(3)—C(5)—C(4)	107·8 (5)	N(3)—C(6)—C(7)	112·6 (5)
C(6)—C(7)—C(8)	115·8 (5)	N(4)—C(8)—C(7)	114·2 (5)
N(4)—C(9)—C(10)	109·5 (4)	N(5)—C(10)—C(9)	110·8 (5)
N(5)—C(11)—C(12)	108·8 (5)	N(1)—C(12)—C(11)	109·5 (5)

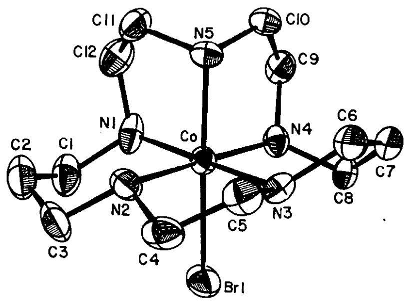

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the complex ion showing atom-numbering scheme.

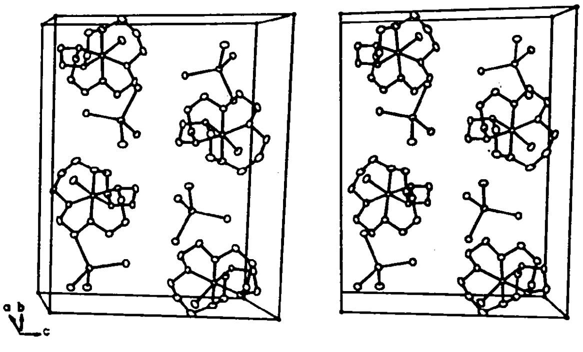

Fig. 2. Stereoscopic view of the molecular packing. Thermal ellipsoids are drawn at the 20% level.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51253 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

N(1)*RS*, N(2)*SR*, N(3)*RS*, N(4)*RS*, N(5) formally achiral (1*RS*, 7*SR*, 11*RS*, 14*RS* in systematic nomenclature). The six-membered chelate ring including N(1) and N(2) has a regular chair conformation while that including N(3) and N(4) has a symmetric skew-boat conformation. The five-membered chelate ring in the equatorial plane containing N(2) and N(3) has a half-chair conformation, while the two axial rings containing N(1), N(5) and N(4), N(5) are best described by an envelope conformation. Some strain within the macrocycle is evidenced by moderate deviations from ideal angles at N and C atoms. For example, in the six-membered rings, the mean of the bond angles at C is 113·6 (5)°, close to the value (113·5°) in the isomeric 17-membered macrocyclic complexes chloro(1,4,7,10,14-pentaazacycloheptadecane)cobalt(III).

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References

Bombieri, G., Forsellini, E., Del Pra, A., Cooksey, C. J., Humanes, M. & Tobe, M. L. (1982). *Inorg. Chim. Acta*, **61**, 43–49.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Curtis, N. F., Gainsford, G., Osvath, P. & Weatherburn, D. C. (1987). *Aust. J. Chem.* **40**, 829–840.

Curtis, N. F., Osvath, P. & Weatherburn, D. C. (1987). *Aust. J. Chem.* **40**, 811–827.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination*. In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Hay, R. W., Bembi, R., McLaren, F. & Moodie, W. T. (1984). *Inorg. Chim. Acta*, **85**, 23–31.

Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

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Structure of *catena*-Poly{[μ-(*N*-acetyl-DL-valinato)-O^1:O^3]-copper(II)}

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Abstract. $[Cu(C_7H_{12}NO_3)_2]_n$, $M_r = 379·9$, triclinic, $P\bar{1}$, $a = 5·687$ (4), $b = 6·224$ (1), $c = 12·634$ (2) Å, $\alpha = 95·48$ (1), $\beta = 89·80$ (4), $\gamma = 98·46$ (4)°, $V = 440·3$ (3) Å^3, $Z = 1$, $D_m = 1·44$ (by flotation), $D_x = 1·43$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 12·7$ cm^{-1}, $F(000) = 199$, $T = 293$ K, $R = 0·053$ from 1514 observed reflections. The Cu atom lies on the symmetry center and displays a square-planar geometry arising from coordination of one carboxylic O and one peptidic O belonging to different ligand molecules, giving rise to a polymeric structure.

Introduction. We have previously observed that on increasing the hydrophobic character of *N*-acetyl amino acids the hydration of the blue binary complex decreases almost regularly. In blue [Cu(*N*-acetylglycinato)$_2$(H$_2$O)$_2$].2H$_2$O (Marcotrigiano, Pellacani, Battaglia & Bonamartini Corradi, 1976) and [Cu(*N*-acetyl-β-alaninato)$_2$(H$_2$O)$_2$] (Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue & Pellacani, 1981) the same essentially square-planar coordination geometry with the CuO$_4$ chromophore is found and the metal environment derives from the carboxylate O atoms of the amino acid molecules, acting as monodentate ligands, and water O atoms. The uncoordinated carboxyl O gives rise to a weak interaction in the out-of-plane axial position, while the peptide group is only involved in hydrogen bonds. *N*-Acetyl-DL-valine forms a blue anhydrous complex for which the electronic spectrum (Marcotrigiano, Menabue & Pellacani, 1980) similarly suggested a square-planar geometry although this is not explained by the usual binding mode of *N*-acetyl amino acids.

Now, in order to verify the probable presence of a new binding mode of this class of ligand, we report here the crystal and molecular structure of *catena*-poly{[μ-(*N*-acetyl-DL-valinato)-O^1:O^3]-copper(II)}.

Experimental.

Preparation of the complex. The complex was prepared by adding a copper(II) perchlorate hexahydrate (1 mmol) solution in anhydrous ethanol to an *N*-acetyl-DL-valine (2 mmol) solution, neutralized with a stoichiometric amount of potassium hydroxide, in anhydrous ethanol. The potassium perchlorate precipitated was filtered off and, on standing for several

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