New Group 2 Metal Hydrazinecarboxylates: a Novel Co-ordination Mode for Hydrazinecarboxylate in a Polymeric, Ten-co-ordinate Barium Complex*

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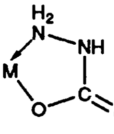
The new hydrazinecarboxylates $[M(O_2CNHNH_2)_2]$ (M = Mg or Sr) and $[Ba(O_2CNHNH_2)_2(N_2H_4)]$ have been prepared. The barium compound is polymeric, each barium centre being ten-co-ordinate and the hydrazinecarboxylate anions displaying a novel co-ordination mode. Each anion is *O,O'*-chelating to one barium, *O*-bridging to a second and bonded to a third barium *via* the terminal nitrogen of the hydrazino moiety. The first two barium cations are also connected by a *N,N'*-bridging hydrazine ligand and the lattice arrangement is cemented by a series of hydrogen bonds.

The solid-state structures of twelve metal hydrazinecarboxylates have been elucidated using single-crystal X-ray crystallography. Five-co-ordinate square-pyramidal geometry is found for $[Zn(O_2CNHNH_2)_2]$,[1] and most other examples, *i.e.* $[Cd(O_2CNHNH_2)_2]$,[2] $[Cd(O_2CNHNH_2)_2(H_2O)]$,[3] $[M(O_2CNHNH_2)_2L_2]$ (M = Mn[4] or Ni,[5] L = H_2O; M = Fe,[6] Co[7] or Zn,[8] L = σ-N_2H_4) and $[N_2H_5][Ni(O_2CNHNH_2)_3]\cdot H_2O$[9] involve six-co-ordinate metal centres. The only examples known to take up higher co-ordination numbers are pentagonal-bipyramidal $[Ca(O_2CNHNH_2)_2]$,[10] one-face-centred pentagonal-bipyramidal $[Ca(O_2CNHNH_2)_2(H_2O)]$[11] and square-antiprismatic $[N_2H_5][Sc(O_2CNHNH_2)_4]\cdot 3H_2O$.[12] Each one contains *N',O*-chelating anions (type **I**), although the anhydrous zinc salt, the two cadmium salts, the two calcium salts and the hydrated manganese salt contain additional *O*-bridging to generate polymeric arrays (type **II**). Here we describe the synthesis and structure of the barium compound $[Ba(O_2CNHNH_2)_2(N_2H_4)]$ which involves the unprecedented co-ordination mode **III**, the anions acting as functionally substituted carboxylates rather than as an isoelectronic structural analogue of glycinate.



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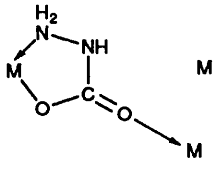

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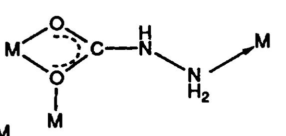

III

Only $[Mg(O_2CNHNH_2)_2(H_2O)_2]$,[13,14] $[N_2H_5][Mg(O_2CNHNH_2)_3]\cdot H_2O$[15] and the two calcium hydrazinecarboxylates mentioned above have been characterised previously for Group 2 metals. One unsuccessful attempt to prepare a strontium compound has been reported.[14] In addition to the barium compound, we therefore report the syntheses of $[M(O_2CNHNH_2)_2]$ (M = Mg or Sr).

Experimental

Hydrazinecarboxylic acid was prepared as previously described.[16] Infrared spectra were recorded as Nujol and hexachlorobutadiene mulls on Perkin Elmer 597 or Nicolet 510P FT spectrophotometers. Finely ground samples held in capillary tubes were used to record Raman spectra on a Spex 1401 spectrometer using an argon-ion laser as the exciting source. Thermal decompositions were studied using a Stanton TR1 thermogravimetric balance, samples being heated in air.

Magnesium Hydrazinecarboxylate.—Carbon dioxide was passed into a suspension of magnesium powder (1.00 g) in hydrazine hydrate (25 cm^3). Heat evolved during the reaction was sufficient to cause boiling of the solution. Carbon dioxide was bubbled through the solution until all the magnesium had been consumed and the reaction mixture had cooled. The resulting colourless solid was filtered off, washed with ethanol and dried *in vacuo*. Yield 1.67 g, 23% (Found: C, 13.5; H, 3.6; N, 32.1. $C_2H_6MgN_4O_4$ requires C, 13.8; H, 3.5; N, 32.1%). IR: 3310s, 3200s [$\nu(NH)$, $\nu(NH_2)$]; 1645vs, 1605vs [$\nu_{asym}(CO_2)$ + $\delta(NH_2)$]; 1470(sh), 1455vs [$\nu_{sym}(CO_2)$]; 1370vs [$\nu(CN)$]; 1190s, 1150(sh) (NH_2 twists); 1065s [$\nu(NN)$]; 802mw, 752mw, 717mw [$\delta(OCO)$]; 645(sh) (NH_2 rock); 585m, 550s cm^{-1} [$\pi(OCO)$].

Magnesium Hydrazinecarboxylate Dihydrate.—*Method A.* Magnesium powder (1.00 g) was suspended in hydrazine hydrate (50 cm^3) and the reactants left open to the atmosphere for 12 d. The colourless solid which formed was filtered off, washed with ethanol and ether and dried *in vacuo*. Yield 8.45 g, 98% (Found: C, 11.4; H, 4.8; N, 27.1. $C_2H_{10}MgN_4O_6$ requires C, 11.4; H, 4.8; N, 26.7%).

Method B. Carbon dioxide was passed for 2 h into a suspension of magnesium powder (1.00 g) in hydrazine hydrate (25 cm^3), cooled in an ice-bath. All the metal reacted, leaving a clear solution to which ethanol (25 cm^3) was added. After leaving overnight surrounded by ice, the resulting solid was filtered off, washed with ethanol and dried *in vacuo*. Yield 6.65 g, 77% (Found: C, 11.5; H, 4.6; N, 26.2%).

Strontium Hydrazinecarboxylate.—To a solution of strontium chloride hexahydrate (1.00 g) in hydrazine hydrate (20 cm^3) was added hydrazinecarboxylic acid (0.59 g). Ethanol was added to the resulting solution until it became just cloudy and then it was left at 0 °C overnight. The colourless crystals which had formed were filtered off, washed with hydrazine hydrate, then ethanol and dried *in vacuo*. Yield 0.51 g, 57% (Found: C, 9.7; H, 2.5; N, 23.7. $C_2H_6N_4O_4Sr$ requires C, 10.1; H, 2.5; N, 23.6%). IR: 3310, 3200s [$\nu(NH)$, $\nu(NH_2)$]; 1650(sh), 1625s, 1570s [$\nu_{asym}(CO_2)$ + $\delta(NH_2)$]; 1470s [$\nu_{sym}(CO_2)$]; 1360s

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Fractional atomic coordinates for $[Ba(O_2CNHNH_2)_2(N_2H_4)]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ba	0.500 00	0.600 00	0.000 00
O(1)	0.384 5(10)	0.494 7(21)	−0.577 6(32)
O(2)	0.379 9(10)	0.280 7(22)	−0.205 2(29)
N(1)	0.525 9(14)	0.955 9(30)	−0.351 1(41)
C(1)	0.339 4(14)	0.356 2(29)	−0.443 6(40)
N(2)	0.249 5(15)	0.290 2(29)	−0.570 1(44)
N(3)	0.200 3(14)	0.340 6(30)	−0.846 0(40)

[ν(CN)]; 1160m (NH_2 twist); 1000m [ν(NN)]; 810m, 720(sh), 710mw [δ(OCO)]; 590m, 560s cm^{-1} [π(OCO)].

Barium Hydrazinecarboxylate–Hydrazine (1/1).—*Method A*. Solid barium chloride dihydrate (1.50 g) was dissolved in refluxing anhydrous hydrazine (40 cm^3) under nitrogen. Carbon dioxide was passed into the solution for 30 min before cooling and standing overnight. The resulting colourless crystals were filtered off, washed with ethanol and dried *in vacuo*. Yield 1.57 g, 80% (Found: C, 7.4; H, 3.0; Ba, 43.1; N, 26.4. $C_2H_{10}BaN_6O_4$ requires C, 7.5; H, 3.1; Ba, 43.0; N, 26.3%).

Method B. Hydrazinecarboxylic acid (0.65 g) was dissolved in a solution of barium chloride dihydrate (1.00 g) in hydrazine hydrate (20 cm^3). Ethanol (10 cm^3) was added and the mixture left overnight at 0 °C. The product was filtered off, washed with hydrazine hydrate, then ethanol and dried *in vacuo*. Yield 0.86 g, 67% (Found: C, 7.7; H, 3.1; N, 26.5%). IR (Raman in parentheses): 3348s, 3276vs, 3244vs, 3187m [ν(NH), ν(NH_2)]; 1596vs, 1578vs (1600m, 1580m) [$\nu_{asym}(CO_2)$ + δ(NH_2)]; 1486vs, 1463vs (1490w) [$\nu_{sym}(CO_2)$]; 1341s (1340m) [ν(CN)]; 1268w, 1247m, 1203w, 1175w, 1139mw (1175w, 1132w) (NH_2 twists); 1068m (1063vs) [ν(NN) hydrazinecarboxylate]; 985w (985w); 947w (953s) [ν(NN) hydrazine]; 921w; 805mw, 725m (720 w) [δ(OCO)]; 656m (660w) (NH_2 rock); 581m (570ms) cm^{-1} [π(OCO)].

X-Ray Structure Determination of $[Ba(O_2CNHNH_2)_2(N_2H_4)]$.—*Crystal data*. $C_2H_{10}BaN_6O_4$, *M* 319.5, monoclinic, space group *C*2, $a = 13.330(3)$, $b = 6.827(1)$, $c = 4.680(2)$ Å, $\beta = 97.63(1)°$, $U = 422.05$ Å^3, $Z = 2$, $D_c = 2.51$ g cm^{-3}, Mo-Kα (graphite-monochromated) radiation, $\lambda = 0.710\,69$ Å, $\mu = 44.1$ cm^{-1}, $F(000) = 304$. Data were collected at room temperature on a Hilger and Watts Y290 diffractometer in the range $2 < \theta < 30°$. A crystal of approximate dimensions 0.2 × 0.2 × 0.25 mm was selected for the structure determination from the filtrate of Method B above, after storage at *ca.* 0 ° C for three weeks. The X-ray diffraction intensities were corrected for Lorentz and polarisation effects and an empirical absorption correction (transmission factor extrema: 1.132, 0.866) was applied.[17] Scattering factors were taken from the usual sources.[18] 588 Reflections were measured, of which 586 were unique with $I \geqslant 3\sigma(I)$. The structure was solved by Patterson methods and refined using the SHELX suite of programs.[19] In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were not included in the refinement as their positions were not manifest in advanced Fourier difference maps. The chiral integrity of the structure, as presented, was greater than 95% based on the Hamilton significance test.[20] Final residuals after ten cycles of least squares were $R = R' = 0.0540$, based on unit weights. The maximum and minimum residual electron densities were 2.3 and −2.2 e Å^{-3}, respectively in the region of the barium and as such have no chemical significance. Final fractional atomic coordinates are given in Table 1, bond lengths and angles in Table 2. The polymeric intermolecular bonding array and the atomic labelling scheme are given in Fig. 1, while Fig. 2 shows the extended hydrogen-bonding network.

Results and Discussion

Hydrated magnesium hydrazinecarboxylate, $[Mg(O_2CNHNH_2)_2(H_2O)_2]$, has been prepared previously by reaction of an aqueous solution of magnesium sulfate with a solution of pre-formed hydrazinium hydrazinecarboxylate[13] or by passing carbon dioxide into a saturated solution of magnesium chloride in hydrazine hydrate.[14] We report here that this compound can also be prepared in high yield directly from magnesium metal. Thus, suspension of the metal powder in hydrazine hydrate followed by prolonged exposure to the atmosphere slowly generates the product. In this reaction atmospheric carbon dioxide is absorbed generating hydrazinecarboxylic acid, which in the presence of excess hydrazine hydrate forms hydrazinium hydrazinecarboxylate. Alternatively, the reaction can be accelerated by using carbon dioxide from a cylinder but then the reaction is extremely vigorous, requiring moderation by cooling in ice.

When the latter reaction is allowed to proceed without cooling, the heat of reaction is sufficient to cause boiling of the hydrazine hydrate with vigorous evolution of hydrogen and the formation of the previously unreported anhydrous salt, $[Mg(O_2CNHNH_2)_2]$, as an insoluble product. Although no magnesium metal remains after the reaction is completed, the yield of the anhydrous compound is only around 25%, the remainder of the magnesium being converted to the more soluble dihydrate. The infrared spectrum of the anhydrous salt (see Experimental section) shows the expected features for a hydrazinecarboxylate and thermogravimetry (heating rate 4 °C min^{-1} in air) indicates that $[Mg(O_2CNHNH_2)_2]$ begins to decompose at 240 °C producing initially $MgCO_3$ which is itself converted to MgO above 360 °C (percentage overall weight loss: found 75.5, calc. 76.9%). The anhydrous compound is also an intermediate in the thermal decomposition of the dihydrate, being produced by heating at 140 °C.

Only one previous, but unsuccessful, attempt to prepare a strontium hydrazinecarboxylate is reported in the literature.[14] We have found that reaction of a solution of $SrCl_2 \cdot 6H_2O$ in hydrazine hydrate with pre-formed hydrazinecarboxylic acid[16] followed by the addition of ethanol gives crystals of anhydrous $[Sr(O_2CNHNH_2)_2]$. This product has an infrared spectrum (see Experimental section) typical of a hydrazinecarboxylate and thermogravimetry shows it to be stable to 230 °C when it starts to decompose to the carbonate which is stable to 1000 °C (percentage overall weight loss: found 37.7, calc. 37.9%).

There have been no previous reports of the existence of a barium hydrazinecarboxylate. We have obtained $[\{Ba(O_2CNHNH_2)_2(N_2H_4)\}_n]$, either by dissolving $BaCl_2 \cdot 2H_2O$ in refluxing anhydrous hydrazine and passing in CO_2, or by treating a solution of $BaCl_2 \cdot 2H_2O$ in hydrazine hydrate with pre-formed hydrazinecarboxylic acid,[16] followed by addition of ethanol. Thermogravimetry shows that decomposition of the product commences at 160 °C, barium carbonate being the sole product at 320 °C with no other detectable intermediates. The carbonate remains unchanged up to 1000 °C (percentage overall weight loss: found 38.0, calc. 38.2%). The vibrational spectrum of the compound indicates the presence of both hydrazinecarboxylate and bridging hydrazine ligands, in particular the detection of two, strong, Raman-active bands at 1063 and 953 cm^{-1} assigned to ν(NN) of the hydrazinecarboxylate and hydrazine moieties, respectively. Polarisability changes of these vibrations will be large relative to those of other vibrations *e.g.* NH_2 deformations which may also occur in this region.

The complex takes up a polymeric structure with a number of striking features. All barium ions are equivalent, as shown in the packing diagram (Fig. 1), and located on two-fold axes intrinsic in the *C*2 space group. The asymmetric unit comprises just one hydrazinecarboxylate anion and one-half of a hydrazine ligand, a C_2 rotation yielding the remaining half of the structure as indicated in Fig. 1 by primed labels. Symmetry-related atoms with doubly and triply primed labels, generated by space-group symmetry transformations, complete the co-ordination sphere

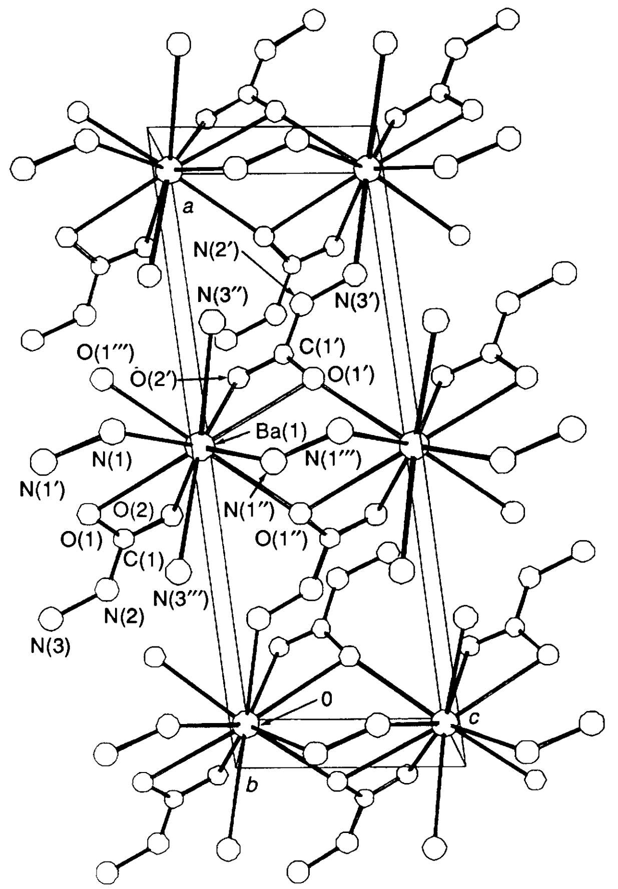

Fig. 1 The co-ordination around barium in [Ba(O$_2$CNHNH$_2$)$_2$-(N$_2$H$_4$)] showing the atom numbering scheme. Atoms O(1′), O(2′), C(1′), N(2′), N(3′) and N(1″) are related to O(1), O(2), C(1), N(2), N(3) and N(1) by operator 1 − *x*, *y*, −*z*. Atoms O(1‴) and N(1′) are related to O(1) and N(1) by operator 1 − *x*, *y*, −(1 + *z*). Atoms O(1″) and N(1‴) are related to O(1) and N(1) by operator *x*, *y*, 1 + *z*. Atom N(3″) is related to N(3) by operator $\frac{1}{2} + x, \frac{1}{2} + y, 1 + z$ and N(3‴) to N(3) by operator $\frac{1}{2} - x, \frac{1}{2} + y, -(1 + z)$

about each barium ion. These ions are ten-co-ordinate, being bonded to six oxygen atoms from two *O,O′*-chelating hydrazinecarboxylates and two bridging oxygens from other hydrazinecarboxylates which are acting as chelates to other barium ions. Four nitrogen atoms from two *N,N′*-bridging hydrazines and two –NHNH$_2$ moieties of still further hydrazinecarboxylates complete the co-ordination sphere. Any attempt at describing the co-ordination geometry around each barium is thwarted by the presence of the two chelating anions with small bites [O(1)–Ba–O(2) 46.0(4)°], but can be regarded as grossly distorted bicapped square antiprismatic with O(1) and O(1′) as the capping atoms. This is not particularly useful, most angles between the antiprismatic barium–donor atom bonds and the axis defined by O(1) or O(1′) deviating considerably from the ideal value of 59.2°.

The co-ordination mode of the hydrazinecarboxylate anions is remarkable. All previous complexes involve co-ordination modes **I** or **II** but this barium complex is the first to involve *O,O′*-chelation of hydrazinecarboxylate groups which therefore behave as carboxylates rather than as amino acidate analogues. A chelating carboxylate-type co-ordination should be uncommon because the four-membered chelate ring presumably would be the least favoured of all the possible co-ordination modes. In addition, one of the chelating oxygen atoms, O(1) or O(1′) in Fig. 1, also acts as a bridging atom to a second barium centre. Examples of carboxylate ligands acting not only in a chelate mode, but also simultaneously as monoatomic bridging ligands, are rare. The structures of [{Cd(O$_2$CMe)$_2$(H$_2$O)$_2$}$_n$],[21] [{Cd(sal)$_2$(H$_2$O)$_2$}$_2$] (sal = salicylate)[22] and [{SnMe$_2$Cl(O$_2$CMe)}$_n$][23] provide examples.

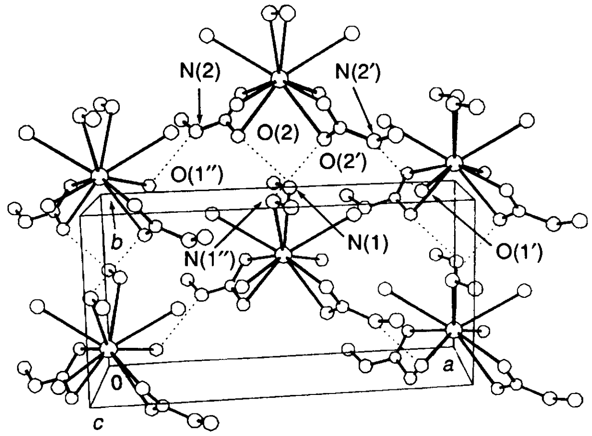

Fig. 2 Packing diagram of [Ba(O$_2$CNHNH$_2$)$_2$(N$_2$H$_4$)], perpendicular to the *ab* plane, illustrating the extended hydrogen bonding present in the lattice

Table 2 Bond lengths (Å) and angles (°) for [Ba(O$_2$CNHNH$_2$)$_2$-(N$_2$H$_4$)] with e.s.d.s in parentheses

Ba–O(1,1′)	3.02(2)	Ba–O(1″,1‴)	2.76(2)
Ba–O(2,2′)	2.80(2)	Ba–N(1,1″)	2.98(2)
Ba–N(3″, 3‴)	3.14(1)	N(1)–N(1′)	1.47(4)
O(1)–C(1)	1.32(3)	C(1)–O(2)	1.28(2)
C(1)–N(2)	1.34(2)	N(2)–N(3)	1.41(3)
Ba–O(1)–C(1)	87.5(1)	Ba–O(2)–C(1)	98.1(1)
Ba–N(1)–N(1′)	116.6(1)	Ba–O(1)–Ba′	108.3(3)
O(1)–Ba–O(2)	46.0(4)	O(1)–C(1)–O(2)	122.3(2)
C(1)–N(2)–N(3)	126.9(2)	N(2)–C(1)–O(1)	117.8(2)
N(2)–C(1)–O(2)	119.8(2)	O(1)–Ba–N(1)	77.5(4)
O(1)–Ba–O(1‴)	64.0(4)	O(1)–Ba–O(1′)	152.4(4)
O(1″)–Ba–N(3‴)	76.2(4)	O(1″)–Ba–N(1)	136.5(4)
O(1″)–Ba–O(1‴)	149.8(4)	O(1″)–Ba–N(3″)	120.8(4)
O(1″)–Ba–N(1″)	72.6(5)	O(1′)–Ba–N(3″)	66.5(4)
N(3″)–Ba–N(3‴)	116.9(4)	O(2)–Ba–N(1)	123.3(4)
O(2)–Ba–O(1‴)	84.2(4)	O(2)–Ba–O(2′)	77.7(4)
O(2)–Ba–O(1′)	108.9(4)	O(2)–Ba–O(1″)	72.2(4)
N(1)–Ba–O(1′)	127.3(5)	N(1)–Ba–N(1″)	70.7(4)
O(1)–Ba–N(3″)	130.4(4)	O(1)–Ba–O(1″)	108.3(4)
Intermolecular distances			
O(1) ··· N(2)	2.84(2)	N(1) ··· O(2)	3.09(2)

The Ba–O distances in the chelate rings are 2.80(2) Å for Ba–O(2) and 3.02(2) Å for Ba–O(1), O(1) also bridging to a second barium cation (generated by the operator *x*, *y*, 1 + *z*) giving rise to a polymeric array parallel to the *z* axis. The Ba–O bridge bonds, Ba–O(1″) and Ba–O(1‴) in Fig. 1, are the shortest of the three types in the structure at 2.76(2) Å. These Ba–O bonds (mean 2.86 Å) are of similar length to those in, for example, nine-co-ordinate barium L-aspartate trihydrate[24] (mean 2.830 Å, excluding the Ba–OH$_2$ interactions). Also, the terminal nitrogen N(3) of each hydrazinecarboxylate acts as a donor to a third proximate barium centre in the lattice generated by lattice centring and ultimately resulting in a polymeric formation parallel to the vector between the origin and the point ($\frac{1}{2}$, $\frac{1}{2}$, 1). The complete co-ordination mode of each anion is as shown in **III**. An additional unidirectional continuous connection between barium cations is achieved by *N,N′*-bridging hydrazine ligands in the *z* direction. The Ba–N (hydrazine) bond lengths, 2.98(2) Å, are shorter than the Ba–N (hydrazinecarboxylate) bond lengths [3.14(1) Å], the mean (3.06 Å) being similar to that for the Ba–N bonds in the triethanolaminato complex $[Ba\{N(CH_2CH_2O)(CH_2CH_2OH)_2\}_2]$.[25]

Close inspection of the packing (Fig. 2) reveals two extended hydrogen-bonding features. Molecules related by unit translations along *y* exhibit polymeric intermolecular hydrogen bonds between N(1) and O(2), and N(1″) and O(2′), respectively, of nearest neighbours [N(1) ··· O(2) 3.09 Å]. Another extended hydrogen-bonding arrangement is to be found along the *x* direction between O(1″) and N(2) of molecules whose coordinates are related by centring [O(1) ··· N(2) 2.84 Å].

As a result of the presence of co-ordination type **III**, several different ring systems are generated in the structure, ranging from four-membered BaOBaO and BaOCO rings, five-membered BaOBaNN rings, seven-membered BaNNBaOCO rings to eight-membered BaOCOBaOCO rings. Adoption of co-ordination mode **III** results in some significant differences in bond lengths and angles when compared to types **I** and **II**. Thus, although the N(2)–N(3) and C(1)–O(2) bond lengths [1.41(3) and 1.28(2) Å respectively] and the N(2)–C(1)–O(1) and O(1)–C(1)–O(2) angles [117.8(2) and 122.3(2)° respectively] are similar to those of all the *N*′,*O*-chelate hydrazinecarboxylates whose structures have been elucidated (mean values 1.41, 1.27 Å and 117 and 125°, respectively), differing N(2)–C(1) bond lengths and N(3)–N(2)–C(1) angles reflect the change in co-ordination type. The N–C bonds are shortened from a mean of 1.38 to 1.34 Å and the N–N–C angles increase from a mean of 119 to 126.9(2)°.

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