Fig. 4. 14-icosahedron unit in $Sc_{44}Os_7$ and $Sc_{44}Ir_7$ in a projection along |110|. The arrangement of the non-shaded icosahedra is similar to that found in the 13-icosahedron unit in $Sc_{57}Rh_{13}$.

isolated tetrahedra. It can be seen from Fig. 4, which shows the 14-icosahedra unit in isotypic $Sc_{44}Ir_7$, that 10 of the 14 icosahedra in the unit are arranged in a similar way to the 13-icosahedra complex shown in Fig. 1(*a*).

In the $Sc_{11}Ir_4$ structure, *cF*120, (Chabot, Cenzual & Parthé, 1980*a*) there are three different sites occupied by Ir atoms: one is at the centre of a cube, the second at the centre of an octahedron and the third one is surrounded by 12 Sc atoms forming a polyhedron which can be considered as intermediate between a cuboctahedron and an icosahedron. These 12-vertex polyhedra share vertices and faces to form a three-dimensional net in which the interstices are occupied by the remaining Ir atoms.

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Structure of Potassium [*meso*-2,3-Butanediaminetetraacetato(4—)]cobalt(III) 2·5 Hydrate, K[Co(C₁₂H₁₆N₂O₈)].2·5H₂O

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Abstract. $M_r = 459·3$, orthorhombic, *Pbcn*, $a = 29·361$ (22), $b = 10·469$ (9), $c = 11·535$ (8) Å, $V = 3545$ (8) Å³, $Z = 8$, $D_m = 1·71$, $D_x = 1·72$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·98$ mm⁻¹, $F(000) = 1896$, room temperature, $R = 0·074$ for 1221 observed reflections $[I \geq 1·96\sigma(I)]$. The structure consists of

octahedral complex anions, K^+ cations and water molecules. The ligand is sexidentate and forms five five-membered chelate rings. Two main sources of strain in the complex anion arise from the fused five-membered chelate rings and repulsion between axial methyl and G-ring methylene hydrogens.

Introduction. Although there are a number of interesting points in the study of the conformations of chelate rings formed by 2,3-butanediaminetetraacetate (2,3-bdta^{4-}), to date no structure of any complex of this sexidentate ligand closely related to ethylenediaminetetraacetate (edta^{4-}) has been reported. Owing to the presence of multiple chiral sites, complexes of 2,3-bdta^{4-} can exist in three diastereomeric forms. As has been revealed by molecular-mechanics calculations (Pavelčik & Majer, 1982), the stereospecific formation of [Co(S,S-2,3-bdta)]$^-$ is expected to take place with a $\Lambda(\Delta\Delta\Delta)$ absolute configuration owing to the preference of the equatorial orientation of two methyl groups to the ethylenediamine chelate ring. In a complex of *meso*-2,3-bdta^{4-}, one of the methyl groups is constrained to be oriented axially, which introduces additional strain into the molecule. Thus, in an effort to examine how this kind of strain affects the bonding and stereochemical parameters of the known [Co(edta)]$^-$ complex (Weakliem & Hoard, 1959), we report here the structure determination of the [Co(*meso*-2,3-bdta)]$^-$ diastereomer, consisting of a racemic mixture of Δ-[Co(R,S-2,3-bdta)]$^-$ and Λ-[Co(R,S-2,3-bdta)]$^-$.

Experimental. D_m by flotation in ethanol/1,2-dibromoethane; crystal $0\cdot30 \times 0\cdot25 \times 0\cdot15$ mm; systematically absent reflections $0kl$ for $k = 2n+1$, $h0l$ for $l = 2n+1$ and $hk0$ for $h+k = 2n+1$ from Weissenberg photographs; Syntex $P2_1$ diffractometer; accurate unit-cell parameters by least-squares refinement of 19 reflections, $8 < \theta < 22°$; intensity data ($h = 0$ to 30, $k = 0$ to 11, $l = 0$ to 12) collected with graphite-monochromatized Mo $K\alpha$ radiation, θ–2θ scan, each reflection scanned at variable rate from $1°$ (in 2θ) below $K\alpha_1$ peak to $1°$ above $K\alpha_2$ maximum, background-to-scan-time ratio $= 1\cdot0$; two standard reflections measured every 100 reflections, 2% average fluctuation throughout data collection; 2334 unique reflections, $2 < \theta \leq 45°$, 1221 with $I \geq 1\cdot96\,\sigma(I)$ considered observed and included in refinement; no absorption correction; trial structure determined by heavy-atom method and refined by block-diagonal least squares, $\Sigma w(\Delta F)^2$ minimized, $w = |F_o|/75$ if $|F_o| < 75$ and $w = 75/|F_o|$ if $|F_o| \geq 75$; anisotropic thermal parameters for all heavy atoms; difference Fourier map revealed positions of all H atoms but one belonging to one of three water molecules lying on twofold axis; H atoms included in refinement with isotropic temperature factors; final $R = 0\cdot074$ and $R_w = 0\cdot065$; final difference Fourier map showed no maxima $> 0\cdot3$ e Å^{-3}; max. $\Delta/\sigma = 0\cdot17$;

Table 1. *Final atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* B_{eq}

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Co	1172 (1)	1583 (2)	1280 (1)	2·33
N(1)	1569 (3)	2973 (10)	902 (9)	2·60
N(2)	1305 (4)	740 (10)	−152 (8)	3·09
O(1)	690 (3)	2572 (8)	694 (7)	2·83
O(2)	1118 (3)	2441 (8)	2734 (7)	2·92
O(3)	1638 (3)	598 (8)	1967 (7)	2·87
O(4)	750 (3)	223 (7)	1483 (7)	2·83
O(5)	509 (3)	4583 (9)	233 (9)	4·70
O(6)	1562 (4)	3553 (10)	3919 (8)	5·17
O(7)	2083 (3)	−1059 (9)	1660 (8)	4·09
O(8)	351 (4)	−1190 (8)	461 (9)	4·57
C(1)	1853 (5)	2478 (13)	−105 (11)	3·01
C(2)	1553 (5)	1706 (14)	−932 (10)	3·12
C(3)	2145 (5)	3482 (14)	−687 (12)	4·09
C(4)	1244 (5)	2432 (14)	−1761 (11)	3·77
C(5)	1286 (4)	4122 (11)	605 (12)	2·71
C(6)	791 (5)	3751 (12)	502 (12)	3·51
C(7)	1826 (4)	3200 (12)	1962 (10)	2·48
C(8)	1479 (4)	3091 (11)	2957 (11)	2·51
C(9)	1612 (5)	−356 (14)	124 (11)	4·11
C(10)	1807 (5)	−308 (11)	1322 (12)	3·19
C(11)	860 (5)	222 (14)	−559 (12)	3·62
C(12)	629 (5)	−333 (12)	522 (11)	3·13
K(1)	−321 (1)	3270 (3)	932 (3)	3·68
O(9)	2886 (4)	1322 (10)	949 (10)	6·00
O(10)	0	−2305 (16)	2500	8·85
O(11)	0	5061 (16)	2500	11·79
O(12)	0	1519 (13)	2500	5·13

scattering factors for uncharged atoms from *International Tables for X-ray Crystallography* (1974); calculations performed with the NRC system (Ahmed, 1970) on a Siemens 4004/150 computer.

Discussion. The final atomic coordinates and equivalent isotropic B's are listed in Table 1.* Table 2 gives bond distances and angles for the complex, which is shown as the Δ-[Co(R,S-2,3-bdta)]$^-$ enantiomer in Fig. 1. The Co atom is bonded octahedrally to two N atoms and to four O atoms from four different carboxylic groups of the complexing molecule. (R,S)-2,3-bdta^{4-} acts as a sexidentate ligand, forming five-membered chelate rings. These are designated here as E, G and R following the notation of Weakliem & Hoard (1959) (see also Fig. 1). The mean Co—N bond distance is $1\cdot915$ (10) Å. The Co—O distances range from $1\cdot878$ (9) to $1\cdot909$ (8) Å, those in the G rings being longer than in the R rings.

There are two main sources of strain in [Co(*meso*-2,3-bdta)]$^-$. The first is common to all edta^{4-} and edta^{4-}-like complexes and arises from the fact that fused five-membered rings in the equatorial plane (plane

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39762 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

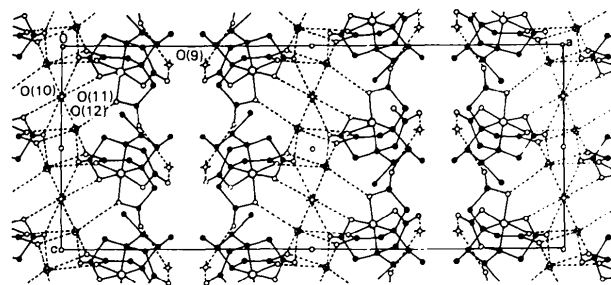Table 2. *Bond distances* (Å) *and angles* (°) *with their e.s.d.'s*

Co—N(1)	1·916 (10)	C(2)—C(4)	1·52 (2)
Co—N(2)	1·913 (10)	C(5)—C(6)	1·51 (2)
Co—O(1)	1·878 (9)	C(6)—O(1)	1·29 (2)
Co—O(2)	1·909 (8)	C(6)—O(5)	1·24 (2)
Co—O(3)	1·890 (9)	C(7)—C(8)	1·54 (2)
Co—O(4)	1·901 (8)	C(8)—O(2)	1·29 (2)
N(1)—C(1)	1·52 (2)	C(8)—O(6)	1·23 (2)
N(1)—C(5)	1·50 (2)	C(9)—C(10)	1·50 (2)
N(1)—C(7)	1·46 (2)	C(10)—O(3)	1·30 (2)
N(2)—C(2)	1·54 (2)	C(10)—O(7)	1·19 (2)
N(2)—C(9)	1·49 (2)	C(11)—C(12)	1·53 (2)
N(2)—C(11)	1·49 (2)	C(12)—O(4)	1·30 (2)
C(1)—C(2)	1·53 (2)	C(12)—O(8)	1·22 (2)
C(1)—C(3)	1·51 (2)		

N(1)—Co—N(2)	91·7 (4)	N(1)—C(1)—C(2)	110 (1)
N(1)—Co—O(1)	87·6 (4)	N(1)—C(1)—C(3)	114 (1)
N(1)—Co—O(2)	83·9 (4)	C(2)—C(1)—C(3)	115 (1)
N(1)—Co—O(3)	93·9 (4)	N(2)—C(2)—C(1)	105 (1)
N(1)—Co—O(4)	173·5 (4)	N(2)—C(2)—C(4)	114 (1)
N(2)—Co—O(1)	95·7 (4)	C(1)—C(2)—C(4)	118 (1)
N(2)—Co—O(2)	172·9 (4)	N(1)—C(5)—C(6)	110 (1)
N(2)—Co—O(3)	87·8 (4)	C(5)—C(6)—O(1)	117 (1)
N(2)—Co—O(4)	84·0 (4)	C(5)—C(6)—O(5)	119 (1)
O(1)—Co—O(2)	89·7 (4)	O(1)—C(6)—O(5)	124 (1)
O(1)—Co—O(3)	176·2 (4)	N(1)—C(7)—C(8)	106 (1)
O(1)—Co—O(4)	88·1 (4)	C(7)—C(8)—O(2)	116 (1)
O(2)—Co—O(3)	87·0 (4)	C(7)—C(8)—O(6)	121 (1)
O(2)—Co—O(4)	101·0 (4)	O(2)—C(8)—O(6)	123 (1)
O(3)—Co—O(4)	90·7 (4)	N(2)—C(9)—C(10)	114 (1)
Co—N(1)—C(1)	104 (1)	C(9)—C(10)—O(3)	114 (1)
Co—N(1)—C(5)	109 (1)	C(9)—C(10)—O(7)	123 (1)
Co—N(1)—C(7)	104 (1)	O(3)—C(10)—O(7)	123 (1)
C(1)—N(1)—C(5)	114 (1)	N(2)—C(11)—C(12)	106 (1)
C(1)—N(1)—C(7)	114 (1)	C(11)—C(12)—O(4)	114 (1)
C(5)—N(1)—C(7)	110 (1)	C(11)—C(12)—O(8)	122 (1)
Co—N(2)—C(2)	107 (1)	O(4)—C(12)—O(8)	124 (1)
Co—N(2)—C(9)	107 (1)	Co—O(1)—C(6)	115 (1)
Co—N(2)—C(11)	105 (1)	Co—O(2)—C(8)	111 (1)
C(2)—N(2)—C(9)	110 (1)	Co—O(3)—C(10)	116 (1)
C(2)—N(2)—C(11)	118 (1)	Co—O(4)—C(12)	114 (1)
C(9)—N(2)—C(11)	108 (1)		
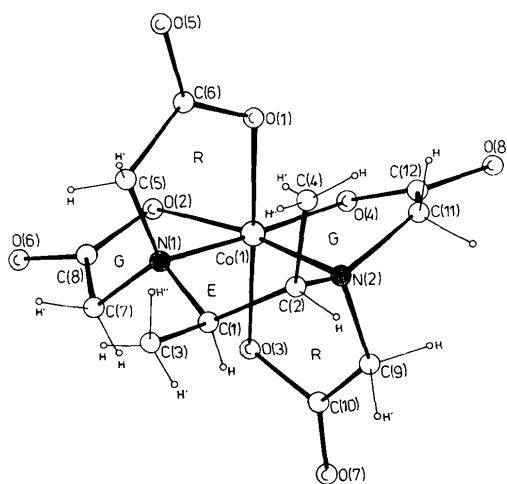
defined by the E ring) cannot open sufficiently to place their donor atoms at the corners of an ideal square. Examination of the molecular model revealed that another source of strain is introduced into the molecule by the C(4) axial methyl group and is represented by repulsion between H(C4) and H(C11) hydrogen atoms (Fig. 1). The relaxation of this close H···H interaction is mainly achieved by a lengthening of the N(2)—C(2) bond and by a widening of the valency angles C(2)—N(2)—C(11), N(2)—C(2)—C(4) and C(1)—C(2)—C(4) (Table 2). Other bond distances and angles (Table 2) not directly affected by strain-minimization considerations are in general normal and closely agree with those reported for the [Co(edta)]⁻.

The C—O distances in all the carboxylate groups are significantly different, as expected. It is interesting to note, however, that the interplay among these distances and the bond angles around C atoms is by no means arbitrary but follows closely the four systematic relationships described by Borthwick (1980).

The overall conformation of the [Co(R,S-2,3-bdta)]⁻ complex may be described as $E,G/R$ following the notation suggested by Porai-Koshits, Pozhidaev & Polynova (1974). The conformations of individual chelate rings have been deduced from the torsion angles and least-squares planes. The central E ring has a slightly distorted twist form of chirality λ. The distortion involves some flattening of the ring at the C(2) atom. All the G rings adopt an envelope conformation with N(1) and N(2) deviating from the mean planes of the remaining four atoms by 0·72 (1) and 0·69 (1) Å, respectively. The conformation of the R rings can also be described as an envelope but the puckering of the rings is much less than that of the G rings. A degree of distortion of chelate rings from planarity may also be measured by the mean deviation of the five atoms of the ring from its least-squares plane. For [Co($meso$-2,3-bdta)]⁻ we find the mean deviation of G and R rings to be 0·18 (1) and 0·06 (1) Å, respectively.

Fig. 1. A perspective drawing of Δ-[Co(R,S-2,3-bdta)]⁻ and the numbering scheme of the atoms and the chelate rings.

Fig. 2. The projection of the structure along the b axis. Inter-molecular hydrogen bonds and ion–dipole interactions are represented by dashed lines. O(10), O(11) and O(12) water oxygens lying on the twofold axes overlap each other in the figure.

The structure projected along the *b* axis is shown in Fig. 2. The complex anions are connected through the K⁺ cations and the molecules of water of crystallization, forming infinite chains parallel to the *c* axis. The chains are held together by van der Waals forces only. The parameters of the hydrogen bonds formed within the chains are given in Table 3. No H atom attached to O(12) of the water molecule was found in the difference synthesis but from the O(12)···O(4) distance (Table 3) this hydrogen bond is also clearly indicated. The K⁺ ion is seven-coordinated to five carboxylic oxygens of three different complex ions: O(1), O(5), O(2) $(-x, y, \frac{1}{2}-z)$, O(5) $(-x, 1-y, -z)$ and O(8) $(-x, -y, -z)$ and to two water molecules O(11) and O(12). The KO₇ polyhedron most closely approximates a monocapped tetragonal bipyramid; the atom O(1) is 'capped' over the face O(5), O(8) and O(12). The K⁺···O distances range from 2·68 (1) to 3·07 (1) Å, mean 2·83 (1) Å, which corresponds to the sum of the ionic radius of K⁺ for coordination number 7 (1·46 Å; Shannon & Prewitt, 1969) and the van der Waals radius of O (1·40 Å).

Table 3. *Hydrogen-bond parameters*

$A-H\cdots B$	$A-H$	$A\cdots B$	$H\cdots B$	Angle $H-A\cdots B$
O(9)–H(O9)···O(7ⁱⁱ)	0·9 (1) Å	2·86 (1) Å	2·1 (1) Å	20 (8)°
O(9)–H'(O9)···O(6ⁱⁱⁱ)	0·9 (1)	2·85 (1)	2·0 (1)	16 (8)
O(10)–H(O10)···O(8ⁱ)	1·1 (1)	2·82 (1)	1·8 (1)	9 (8)
O(11)–H(O11)···O(10ⁱ)	1·0 (2)	2·76 (2)	2·4 (2)	61 (10)
O(12)···O(4ⁱ)	—	2·84 (1)	—	—

Symmetry code for B: (i) x, y, z; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$.

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Structure of Bis(*O,O'*-diisopropyl phosphorodithioato)nickel(II), Ni[S₂P(O'C₃H₇)₂]₂

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Abstract. $M_r = 485\cdot29$, monoclinic, $C2/c$, $a = 14\cdot047$ (2), $b = 10\cdot338$ (3), $c = 16\cdot807$ (3) Å, $\beta = 109\cdot71$ (1)°, $U = 2298$ (2) Å³, $D_m = 1\cdot36$ (2), $Z = 4$, $D_x = 1\cdot402$ (1) Mg m⁻³, Ni-filtered Cu Kα radiation, $\lambda = 1\cdot5418$ Å, μ(Cu Kα) = 5·86 mm⁻¹, $T = 295$ (2) K, $F(000) = 1016$, $R = 0\cdot065$ for 1751 observed reflections with $I \geq 3\sigma(I)$. Crystals contain discrete molecules of the title compound with the two dithiophosphate ligands chelating the Ni atom in the expected square-planar array with equivalent Ni–S distances of average value 2·221 (1) Å.

Introduction. Nickel(II) dithiophosphates and dithiophosphinates of the general formula Ni(*RR'*dtp)₂ have been the subject of extensive crystallographic studies. Amongst the complexes which have been structurally characterized are the following: (i) *R*=*R'*: CH₃ (Jones, Ansell & Katz, 1969), CH₂CH₃ (Shetty & Fernando, 1969), C₆H₅ (Porta, Sgamellotti & Vinciguerra, 1968), OCH₃ (Kastalsky & McConnell, 1969), OCH₂CH₃

(Fernando & Green, 1967; McConnell & Kastalsky, 1967); and (ii) *R*≠*R'*: CH₃, C₄H₃S (Wunderlich & Wussow, 1979), CH₃, CH₂CH₃ (Wunderlich, 1980), and CH₃, N(CH₃)₂ (Seel & Zindler, 1980). In all of the above structures the 1,1-dithiolate ligand chelates the Ni atom with equivalent Ni–S bonds. Recently the structure of the Niᴵᴵ complex where *R*=CH₂CH₃, *R'*=O'C₃H₇ (1) has been reported (Bone, Sowerby, Constantinescu & Haiduc, 1979) in which marked asymmetry is apparent in the mode of coordination of the dithiophosphate ligand: Ni–S 2·262 (1) and 2·116 (1) Å. When *R*=*R'*=CH₂CH₃ (Shetty & Fernando, 1969) no special features are observed in the structure to account for this anomalous chelation and it was therefore of interest to ascertain whether the unusual coordination mode noted for (1) is due to the influence of the relatively bulky isopropyl substituents. We therefore have undertaken a crystal structure determination of the Niᴵᴵ complex where *R*=*R'*=O'C₃H₇, hereafter Ni{(C₃H₇O)₂dtp}₂.