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Potassium *trans*-Bis(*tert*-butyliminodiacetato)chromate(III) Tetrahydrate

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Abstract. $K[Cr(C_8H_{13}NO_4)_2].4H_2O$, $K^+.C_{16}H_{26}CrN_2O_8^-.4H_2O$, monoclinic, $P2_1/c$, $a = 7{\cdot}870\,(1)$, $b = 19{\cdot}707\,(3)$, $c = 7{\cdot}921\,(1)$ Å, $\beta = 107{\cdot}84\,(1)°$, $Z = 2$, $D_m = 1{\cdot}513$, $D_x = 1{\cdot}527$ Mg m^{-3}, $M_r = 537{\cdot}5$, μ(Mo $K\alpha$) = 0·75 mm^{-1}, $R = 0{\cdot}035$. The Cr atom is located at a center of symmetry with a *trans* configuration of the N atoms. The coordination of the Cr atom is distorted octahedral. The water molecules form a system of hydrogen bonds. Preliminary results have been reported [Wunderlich & Mootz (1977). Fourth Eur. Crystallogr. Meet., Oxford, England, Abstract PI.64].

Introduction. The synthesis and characterization of the title compound have been reported by Wernicke, Schmidtke & Hoggard (1977). Violet crystals were grown from aqueous solution. Systematic absences were unique for the space group $P2_1/c$. The intensities of all symmetry-independent reflections up to $2\theta = 55°$ (Mo $K\alpha$ radiation, crystal monochromator) were determined with an automatic diffractometer (Syntex $P2_1$) with the ω-scan technique. From the resulting 2630 intensities 2206 were classified as observed ($F > 3\sigma_F$) and were used for the structure determination. With independent Cr and K atoms, at 0,0,0 and $\frac{1}{2},0,\frac{1}{2}$ respectively, the much larger observed average $|F|$ for hkl all even or all odd, as compared to the remaining reflections, is explained. Phasing with these atoms produced the whole structure. After initial refinement all H atoms could be gained from difference syntheses and were included with isotropic temperature factors in the final refinement with 216 variables converging at $R = 0{\cdot}035$ (0·044) and $R_w = 0{\cdot}042$ (0·044) for the observed (all) reflections. Weights were derived from counter statistics by $1/w = \sigma_F^2 + 0{\cdot}0004F^2$; scattering factors were taken from Cromer & Waber (1974). The final positional parameters are listed in Tables 1 and 2.* All calculations were carried out with the program system *EXTL* (Syntex) on an Eclipse computer (Data General) with 32 K memory.

Table 1. *Positional parameters* (×10^4) *of the non-hydrogen atoms with e.s.d.'s resulting from the least-squares refinement in parentheses*

The equivalent isotropic temperature factors, B_{eq} (Å^2), have been calculated by $B_{eq} = \frac{1}{3}(B_{11}a^{*2}a^2 + B_{12}a^*b^*ab\cos\gamma\ldots)$.

	x	y	z	B_{eq}
K	5000	0	5000	2·90
Cr	0	0	0	1·31
O(1)	−1731 (2)	−403 (1)	1020 (2)	2·12
O(2)	−1875 (2)	295 (1)	−2160 (2)	2·02
O(5)	−3886 (2)	−194 (1)	2217 (2)	2·94
O(6)	−3019 (2)	1202 (1)	−3751 (2)	3·27
N	−869 (2)	932 (1)	888 (2)	1·73
C(1)	−2773 (2)	1 (1)	1527 (2)	2·01
C(2)	−2624 (3)	749 (1)	1152 (3)	2·26
C(3)	−1246 (3)	1366 (1)	−726 (2)	2·24
C(4)	−2128 (3)	942 (1)	−2358 (2)	2·17
C(5)	370 (3)	1288 (1)	2543 (2)	2·33
C(6)	−334 (4)	1996 (1)	2791 (3)	3·56
C(7)	2227 (3)	1360 (1)	2337 (3)	3·02
C(8)	465 (3)	861 (1)	4181 (3)	3·01
O*w*(1)	−3338 (4)	−1798 (1)	1539 (4)	6·86
O*w*(2)	−5088 (4)	−2409 (1)	3612 (4)	6·36

Table 2. *Positional parameters* (×10^3) *and temperature factors* (Å^2) *of the* H *atoms with e.s.d.'s in parentheses*

The H atoms are bonded to O and C atoms of identical first digit of their numbering.

	x	y	z	B
H(21)	−358 (3)	85 (1)	−1 (3)	2·7 (4)
H(22)	−287 (3)	102 (1)	210 (3)	4·1 (6)
H(31)	−7 (3)	153 (1)	−85 (3)	3·0 (5)
H(32)	−201 (3)	172 (1)	−68 (3)	2·6 (4)
H(61)	49 (3)	218 (1)	389 (4)	4·1 (6)
H(62)	−31 (4)	230 (1)	183 (4)	4·8 (6)
H(63)	−152 (4)	197 (2)	288 (4)	5·1 (7)
H(71)	222 (3)	166 (1)	135 (3)	3·9 (6)
H(72)	299 (4)	155 (1)	336 (4)	4·6 (6)
H(73)	268 (3)	92 (1)	212 (3)	3·4 (5)
H(81)	78 (3)	41 (1)	406 (3)	3·6 (5)
H(82)	138 (3)	104 (1)	522 (3)	4·0 (6)
H(83)	−60 (4)	87 (1)	455 (4)	4·5 (6)
H*w*(11)	−397 (5)	−194 (2)	238 (5)	8·2 (11)
H*w*(12)	−322 (7)	−137 (3)	174 (7)	11·9 (16)
H*w*(21)	−483 (5)	−262 (2)	464 (5)	8·0 (11)
H*w*(22)	−587 (5)	−211 (2)	398 (5)	7·9 (10)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35051 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. The title compound is a member of a series of crystal structures of Cr^{III} complexes with iminodiacetic acid and different alkyl residues *R* at the N atom: $[Cr\{RN(CH_2COO)_2\}_2]^-$. In all structures the influence of the residue on the geometry of the octahedral environment of the Cr atom, in particular the choice between a *cis* and a *trans* configuration for the two N atoms, is of interest. The smallest substituent *R* = H yielded a *cis* configuration (Mootz & Wunderlich, 1980*a*), while $R = i\text{-}C_3H_7$ shows a *trans* configuration (Mootz & Wunderlich, 1980*b*).

The anion of the title compound with main bond lengths is given in Fig. 1, the corresponding bond angles are listed in Table 3. In agreement with the point symmetry $\bar{1}$ of the anion, the configuration is *trans*. The spacious alkyl residue and ring constraints determine the geometry of the molecule. The octahedral coordination of the Cr atom deviates by up to 11·3° from ideal angles. The Cr—O bond lengths of 1·953 and 1·974 Å agree with the values for the other structures of this series, but the Cr—N distance is elongated because of the size of the substituent at the N atom: 2·058 and 2·070 (*R* = H), 2·118 ($R = i\text{-}C_3H_7$), and 2·152 Å ($R = tert\text{-}C_4H_9$). The increase can be followed spectroscopically through its weakening influence on the ligand field (Wernicke, Schmidtke & Hoggard, 1977) and is confirmed in the discussion of the crystal structure of rubidium bis(pyridine-2,6-dicarboxylato)chromate(III) (Fürst, Gouzerh & Jeannin, 1979). The two symmetry-independent five-membered rings deviate by up to 0·2 [involving O(1)] and 0·3 Å [involving O(2)] from planarity. The angles at the tetrahedral N atoms range from 102·1 to 119·0°. Bond lengths and angles involving H atoms are in the expected ranges (0·93–1·01 Å, 103–115°) and are not listed.

O(2) and O(6) of one of the two independent carboxylate groups and O(5) of the other one in another anion form three independent contacts <2·85

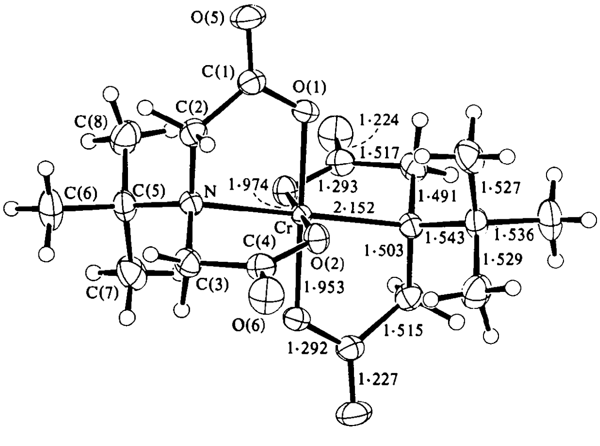

Fig. 1. The anion of $K[Cr\{tert\text{-}C_4H_9N(CH_2COO)_2\}_2].4H_2O$ with bond lengths (Å). The e.s.d.'s are 0·001 Å for Cr--O and Cr—N and 0·002–0·003 Å for the other bond lengths. The Cr atom is located at a center of symmetry. The heavy atoms are represented by thermal ellipsoids of 50% probability (*ORTEP* II, Johnson, 1976). The temperature factor of the H atoms is set to $B = 0{\cdot}67$ Å^2.

Table 3. *Bond angles and non-bonding distances of* $K[Cr\{tert\text{-}C_4H_9N(CH_2COO)_2\}_2].4H_2O$

Cr and K atoms are located at centers of symmetry.

Symmetry code: (i) *x*, *y*, *z* + 1.

(*a*) Angles (°) of the complex anion

The e.s.d.'s are 0·1° at Cr, O and N, and 0·2° at C atoms.

O(1)—Cr—O(2)	92·7	C(3)—N—C(5)	112·0
O(1)—Cr—N	83·1	N—C(3)—C(4)	109·4
O(2)—Cr—N	78·7	C(3)—C(4)—O(2)	115·3
Cr—O(1)—C(1)	117·9	C(3)—C(4)—O(6)	121·6
O(1)—C(1)—C(2)	116·3	O(6)—C(4)—O(2)	123·2
O(1)—C(1)—O(5)	123·5	C(4)—O(2)—Cr	116·2
O(5)—C(1)—C(2)	120·1	N—C(5)—C(6)	111·3
C(1)—C(2)—N	113·0	N—C(5)—C(7)	109·1
Cr—N—C(2)	103·8	N—C(5)—C(8)	108·9
Cr—N—C(3)	102·1	C(6)—C(5)—C(7)	109·0
Cr—N—C(5)	119·0	C(6)—C(5)—C(8)	108·5
C(2)—N—C(3)	107·9	C(7)—C(5)—C(8)	110·0
C(2)—N—C(5)	111·1		

(*b*) Distances (Å) involving the K^+ ion

The e.s.d.'s are 0·001–0·002 Å.

K—O(2^i)	2·838	K—O(5)	2·638
K—O(6^i)	2·842		

(*c*) Angles (°) at the K^+ ion

The e.s.d.'s are 0·1°.

O(2^i)—K—O(5)	105·3	O(5)—K—O(6^i)	97·2
O(2^i)—K—O(6^i)	45·9		

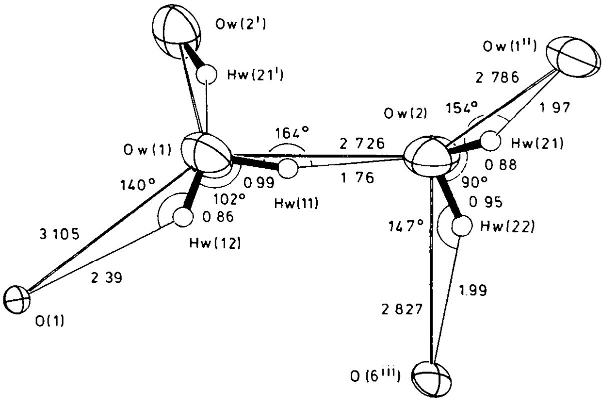

Fig. 2. Geometry of the water molecules and hydrogen bonds with thermal ellipsoids of 25% probability. The e.s.d.'s are: 0·004 Å (O···O), 0·04–0·06 Å (O—H, H···O), and 4° (O—H···O, H—O—H). Symmetry code: (i) $x, -\frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (iii) $-1-x, -y, -z$.

Å to the K^+ ion at a center of symmetry in a very distorted octahedral coordination (Table 3). The geometry of the hydrogen bonds formed by the two symmetry-independent water molecules is shown in Fig. 2. All four hydrogen bonds are of the type O—H···O with distances and angles in the usual range except O*w*(1)—H*w*(12)···O(1), which shows elongated distances to the acceptor O(1), but still may be considered as a hydrogen bond. The water molecules form infinite chains along *c* and link the complex anions into a three-dimensional array.

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$(-)_{579}$-Bis[(*S*)-(+)-*O*,*O*′-(1,1′-binaphthyl-2,2′-diyl)dithiophosphato]nickel(II)

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Abstract. $[Ni(C_{20}H_{12}O_2PS_2)_2]$, $C_{40}H_{24}NiO_4P_2S_4$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}630\ (3)$, $b = 10{\cdot}171\ (4)$, $c = 37{\cdot}489\ (13)$ Å, $Z = 4$, $D_m = 1{\cdot}44$, $D_x = 1{\cdot}48$ Mg m^{-3}, μ(Cu $K\alpha$) = 3·92 mm^{-1}, $M_r = 817{\cdot}5$. The structure was refined to $R = 0{\cdot}05$ and the absolute configuration determined. The Ni atom is coordinated by four S atoms in a square. The dihedral angles of the C—C bonds bridging the two naphthyl residues in each half of the molecule are +53·5 and +52·1° and define an (*S*,*S*) configuration.

Introduction. The technical application of several metal complexes of dithiophosphoric acid has become of interest during recent years (Wasson, Woltermann & Stoklosa, 1973). The crystal structures of two dithiophosphatonickel(II) complexes, $[Ni(S_2PR_2)_2]$, with all four substituents *R* identical, have been reported: $R = C_2H_5O$ (McConnell & Kastalsky, 1967) and $R = CH_3O$ (Kastalsky & McConnell, 1969). The title compound is the first dithiophosphato complex of Ni^{II} with a bidentate ligand of axial chirality, introduced as one enantiomer only. The preparation and preliminary structural results have been reported by Hoffmann, Kuchen, Poll & Wunderlich (1979) and Poll, Wunderlich & Wussow (1979).

The complex crystallizes from toluene on addition of hexane without a characteristic habit; its color is between brown and violet. Systematic absences are unique for the space group $P2_12_12_1$. The lattice parameters were determined from 15 optimized diffractometer angles by least-squares refinement. The intensities of all symmetry-independent reflections up to $2\theta = 135°$ were measured with Cu $K\alpha$ radiation (crystal monochromator) in an ω-scan mode on an automated diffractometer (Syntex $P2_1$). 2928 out of 3796 reflections were classified as observed ($F > 3\sigma_F$) and were used for the structure determination. The phase problem was solved by the Patterson function. All H atoms could be located from difference maps. The anomalous dispersion of Ni, S, and P was used to determine the absolute configuration. The refinement (556 parameters) converged at $R = 0{\cdot}055$ (0·074) and $R_w = 0{\cdot}053$ (0·056) for the observed (all) reflections. The corresponding refinement of the inverted molecule converged at a significantly larger R_w of 0·057 (0·060), precluding that configuration at the 99·5% probability level (Hamilton, 1974). Weights were derived from counting statistics by $1/w = \sigma_F^2 + 0{\cdot}0004F^2$. Scattering factors were taken from Cromer & Waber (1974). All calculations were performed with the system *EXTL*

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