

Potassium *cis*-Bis(iminodiacetato)chromate(III) Trihydrate

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Abstract. $K[Cr\{HN(CH_2COO)_2\}_2] \cdot 3H_2O$, $C_8H_{10}CrN_2O_8 \cdot K^+ \cdot 3H_2O$, orthorhombic, *Pbcn*, $a = 18.721$ (4), $b = 10.286$ (2), $c = 15.719$ (3) Å, $Z = 8$, $D_m = 1.763$, $D_x = 1.788$ Mg m⁻³, $M_r = 407.3$, $\mu(Mo K\alpha) = 1.12$ mm⁻¹. Final $R = 0.076$. The structure is almost isotopic with that of the analogous Co^{III} complex which has only 2.5 water molecules. Two iminodiacetate ions form a distorted octahedral coordination of the Cr atom with the N atoms in a *cis* configuration. Preliminary results have been reported [Wunderlich & Mootz (1977). 4th Eur. Crystallogr. Meet., Oxford, England, Abstr. PI.64].

Introduction. A spectroscopic investigation of the title compound has been reported by Hoggard & Schmidtke (1972). Crystallization from aqueous solution yielded orthorhombic prisms of deep-red colour. From systematic absences the space group *Pbcn* was determined with one formula in the asymmetric unit. The intensities of all 3473 symmetry-independent reflections up to $2\theta = 55^\circ$ (Mo $K\alpha$ radiation, crystal monochromator) were collected with a computer-controlled diffractometer (Syntex P2₁) and an ω scan. 2148 reflections were classified as observed ($F > 3\sigma_F$) and were used for the determination of the structure. The phase problem was solved by the heavy-atom method localizing the Cr and K atoms by the Patterson function. All H atoms of the complex anion were determined by a difference synthesis. The final refinement, with anisotropic temperature factors for non-H atoms and isotropic for H (257 parameters), converged at $R = 0.076$ (0.132) and $R_w = 0.069$ (0.077) for the observed (all) reflections. The weighting scheme was $1/w = \sigma_F^2 + (0.02F)^2$; scattering factors were taken from Cromer & Waber (1974). The final positional parameters are listed in Tables 1 and 2.* All calculations were carried out on a 32K computer (ECLIPSE, Data General) with EXTL (Syntex).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34839 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$) for the non-hydrogen atoms with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
K	4383 (1)	-2318 (2)	-1503 (1)
Cr	2446 (1)	57 (1)	973 (1)
O(1)	3012 (2)	-173 (4)	-64 (3)
O(2)	1808 (2)	1396 (4)	500 (3)
O(3)	1866 (2)	48 (5)	2010 (3)
O(4)	3127 (2)	1356 (4)	1379 (3)
O(5)	3064 (3)	-1087 (5)	-1341 (3)
O(6)	692 (3)	1720 (6)	76 (3)
O(7)	1696 (3)	-840 (5)	3280 (3)
O(8)	4244 (3)	1604 (6)	1833 (3)
N(1)	1756 (3)	-1185 (5)	358 (4)
N(2)	3079 (3)	-1199 (6)	1674 (4)
C(1)	2766 (3)	-916 (6)	-668 (4)
C(2)	2071 (4)	-1600 (7)	-470 (4)
C(3)	1072 (4)	-478 (8)	280 (7)
C(4)	1187 (4)	995 (7)	278 (4)
C(5)	2053 (4)	-710 (7)	2633 (4)
C(6)	2737 (4)	-1462 (8)	2513 (5)
C(7)	3798 (4)	-537 (8)	1731 (6)
C(8)	3733 (3)	934 (7)	1658 (4)
Ow(1)	527 (3)	4844 (9)	4415 (5)
Ow(2)	330 (4)	2512 (8)	3723 (7)
Ow(3)	214 (5)	9390 (10)	2407 (14)
Ow(4)	677 (7)	1580 (15)	2477 (13)

Table 2. Positional parameters ($\times 10^3$) of the hydrogen atoms excluding the water molecules with e.s.d.'s in parentheses

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

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	171 (3)	-194 (6)	70 (4)
H(2)	315 (3)	-183 (5)	149 (3)
H(21)	171 (3)	-136 (6)	-86 (3)
H(22)	216 (3)	-257 (5)	-45 (3)
H(31)	80 (4)	-63 (7)	-23 (5)
H(32)	81 (5)	-56 (9)	84 (6)
H(61)	258 (4)	-229 (7)	249 (4)
H(62)	309 (4)	-125 (8)	303 (5)
H(71)	399 (3)	-83 (6)	218 (4)
H(72)	412 (4)	-79 (8)	110 (5)

The space group *Pbcn* requires systematic absences of $0kl$ with $k = 2n + 1$. However, in the data set there were 22 weak reflections of this class with $3\sigma_F \leq F \leq 12 \cdot 5\sigma_F$. This would require a reduction of the symmetry leading to the space group *Pna2₁* (exchange of axes *a* and *c*) with two molecules in the asymmetric unit. Probably the deviation from the higher symmetry is caused only by the arrangement of the water molecules which can be described in the space group *Pbcn* only with unusually large thermal motion and a disorder of two O atoms. A refinement in *Pna2₁* failed. Because the complex anion seems not to be affected by this problem its approximate treatment and description in *Pbcn* appears justified.

Discussion. The iminodiacetate anion, $\text{HN}(\text{CH}_2\text{COO}^-)_2$, as a facial terdentate ligand forms stable 2:1 octahedral complexes with many transition-metal ions. With respect to the two N atoms, *cis* and *trans* configurations have been observed: for example $\text{K}[\text{Co}\{\text{HN}(\text{CH}_2\text{COO})_2\}_2] \cdot 2 \cdot 5\text{H}_2\text{O}$ is *cis* (Corradi, Palmieri, Nardelli, Pellinghelli & Vidoni Tani, 1973) while $\text{Li}_2[\text{Ni}\{\text{HN}(\text{CH}_2\text{COO})_2\}_2] \cdot 4\text{H}_2\text{O}$ is *trans* (Mammano, Templeton & Zalkin, 1977). The title compound, apart from differences in the water structure, is isotopic with the corresponding Co^{III} complex cited above; in particular the N atoms are in a *cis* configuration. This is in agreement with the spectroscopic study of Hoggard & Schmidtke (1972).

Fig. 1 shows the anion with main bond lengths; bond angles are listed in Table 3. The octahedron around the Cr atom is distorted by up to $12 \cdot 8^\circ$ from ideal values

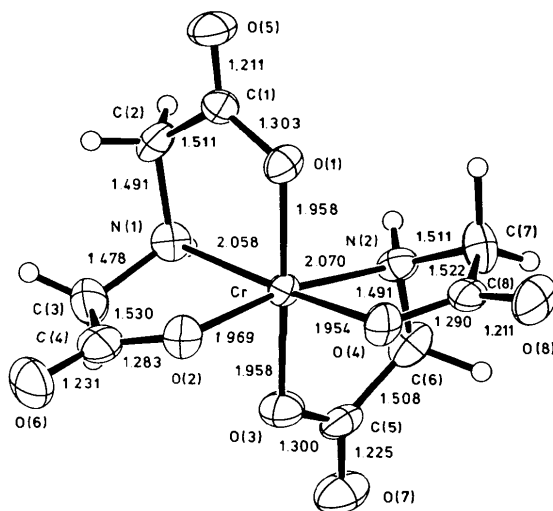


Fig. 1. The complex anion of $\text{K}[\text{Cr}\{\text{HN}(\text{CH}_2\text{COO})_2\}_2] \cdot 3\text{H}_2\text{O}$ in arbitrary crystallographic orientation with bond lengths (Å). The e.s.d.'s are: Cr—O, Cr—N 0.004–0.006; C—O, C—N, C—C 0.008–0.011 Å. The heavy atoms are represented by thermal ellipsoids of 50% probability (ORTEP II, Johnson, 1976). The isotropic temperature factor of the H atoms is set to $B = 0.67 \text{ Å}^2$.

Table 3. Bond angles and non-bonding distances in $\text{K}[\text{Cr}\{\text{HN}(\text{CH}_2\text{COO})_2\}_2] \cdot 3\text{H}_2\text{O}$

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

(a) Angles ($^\circ$) of the complex anion

The e.s.d.'s are 0.2 $^\circ$ at Cr, 0.4 $^\circ$ at O, 0.4–0.6 $^\circ$ at N and 0.6–0.7 $^\circ$ at C atoms.

O(1)—Cr—O(2)	95.6	C(2)—N(1)—C(3)	114.2
O(1)—Cr—O(3)	172.8	Cr—N(1)—C(3)	106.2
O(1)—Cr—O(4)	90.1	N(1)—C(3)—C(4)	111.4
O(1)—Cr—N(1)	82.7	C(3)—C(4)—O(2)	116.5
O(1)—Cr—N(2)	93.4	C(3)—C(4)—O(6)	119.6
O(2)—Cr—O(3)	88.9	O(6)—C(4)—O(2)	123.9
O(2)—Cr—O(4)	92.3	C(4)—O(2)—Cr	115.3
O(2)—Cr—N(1)	82.9	Cr—O(3)—C(5)	118.7
O(2)—Cr—N(2)	169.9	O(3)—C(5)—C(6)	116.2
O(3)—Cr—O(4)	95.4	O(3)—C(5)—O(7)	123.0
O(3)—Cr—N(1)	92.3	O(7)—C(5)—C(6)	120.7
O(3)—Cr—N(2)	82.6	C(5)—C(6)—N(2)	112.5
O(4)—Cr—N(1)	170.9	C(6)—N(2)—Cr	109.8
O(4)—Cr—N(2)	83.1	C(6)—N(2)—C(7)	114.3
N(1)—Cr—N(2)	102.8	Cr—N(2)—C(7)	105.1
Cr—O(1)—C(1)	119.1	N(2)—C(7)—C(8)	111.8
O(1)—C(1)—C(2)	115.3	C(7)—C(8)—O(4)	115.5
O(1)—C(1)—O(5)	124.0	C(7)—C(8)—O(8)	119.0
C(2)—C(1)—O(5)	120.7	O(8)—C(8)—O(4)	125.5
C(1)—C(2)—N(1)	112.7	C(8)—O(4)—Cr	117.0
C(2)—N(1)—Cr	109.9		

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

The e.s.d.'s are 0.005 Å in distances to O atoms and 0.010 Å to Ow atoms. Only one of the two Ow(3) positions around a K^+ ion is occupied.

$\text{K}^+ \cdots \text{O}(5)$	2.787	$\text{K}^+ \cdots \text{O}(8^{\text{iv}})$	2.724
$\text{K}^+ \cdots \text{O}(6^{\text{i}})$	2.675	$\text{K}^+ \cdots \text{Ow}(1^{\text{v}})$	2.930
$\text{K}^+ \cdots \text{O}(7^{\text{ii}})$	2.790	$\text{K}^+ \cdots \text{Ow}(3^{\text{v}})$	2.836
$\text{K}^+ \cdots \text{O}(8^{\text{iii}})$	2.730	$\text{K}^+ \cdots \text{Ow}(3^{\text{vi}})$	2.996

(c) Angles ($^\circ$) at the K^+ ion

The e.s.d.'s are 0.2–0.4 $^\circ$.

	O(5)	O(6 ⁱ)	O(7 ⁱⁱ)	O(8 ⁱⁱⁱ)	O(8 ^{iv})	Ow(1 ^v)	Ow(3 ^v)
O(6 ⁱ)	92.1						
O(7 ⁱⁱ)	71.2	80.0					
O(8 ⁱⁱⁱ)	83.2	169.6	89.8				
O(8 ^{iv})	137.0	109.0	147.5	80.5			
Ow(1 ^v)	67.1	82.4	133.7	104.1	78.8		
Ow(3 ^v)	129.2	107.3	67.0	69.4	80.6	159.1	
Ow(3 ^{vi})	145.7	101.8	80.5	77.7	67.2	145.2	16.5

of 90 and 180 $^\circ$. The averaged bond lengths at the Cr atom are: Cr—O 1.960, Cr—N 2.064 Å. The two iminodiacetate ions form four five-membered rings at the Cr atom. The two rings involving O(1) and O(3) are planar within 0.03 Å while the other two involving O(2) and O(4) (Fig. 1) are puckered by up to 0.2 Å from the least-squares planes. The H atoms show the expected geometry.

The K^+ ion is coordinated in an irregular geometry by seven O atoms at distances up to 3 Å. The four O atoms of the acetate group reveal short $\text{K}^+ \cdots \text{O}$ distances (average 2.74 Å), while the water molecules form longer $\text{K}^+ \cdots \text{Ow}$ distances (average 2.92 Å).

Distances and angles at the K⁺ ion are given in Table 3.

The arrangement of the water molecules in space group *Pbcn* requires half-atom positions Ow(3) and Ow(4) for one water molecule, which cause a few forbidden O...O distances of less than 2.3 Å. Besides this, many possible hydrogen bonds can be recognized which determine the three-dimensional arrangement of the structure. Possibly a reduction of the symmetry may lead to an ordered structure of the water molecules.

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Bis(trichlorovinyl)mercury–3,4,7,8-Tetramethyl-1,10-phenanthroline

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Abstract. [Hg(C₂Cl₃)₂].C₁₆H₁₆N₂. C₄Cl₆Hg.C₁₆H₁₆N₂. *M_r* = 697.68, monoclinic, *C2/c*, *a* = 18.976 (6), *b* = 13.876 (4), *c* = 18.401 (5) Å, β = 107.32 (6)°, *U* = 4625.5 Å³, Mo *K*_α, λ = 0.71069 Å, *Z* = 8, *D_m* = 1.98 (2), *D_c* = 2.00 Mg m⁻³, μ = 7.06 mm⁻¹, *F*(000) = 2656. The structure was refined to *R* = 0.052 for 4158 counter reflections. There is a weak but significant donor–acceptor interaction between the 3,4,7,8-tetramethyl-1,10-phenanthroline ligand and bis(trichlorovinyl)mercury. Long Hg–N distances [2.687 (6), 2.629 (9) Å] are accompanied by a small N–Hg–N angle of 61.4 (2)° and distortion of the C–Hg–C skeleton from linearity [164.8 (3)°].

Introduction. In contrast to dialkylmercurials for which no addition complexes have been isolated, dialkynylmercurials give rise to stable adducts with, for example, nitrogenous bases (Cano-Esquivel, Santos-Macias & Ballester-Reventos, 1977). Dialkenylmercurials might also be expected to form stable complexes and while the coordination chemistry of the dialkenylmercurials themselves has not been reported, bis(trichlorovinyl)mercury is known (Bell, Nowell & Reynolds, 1979) to form isolable adducts of the type [Hg(Cl₂C=CCl)₂].*L* [*L* = 1,10-phenanthroline (phen); 2,9-dimethyl-1,10-phenanthroline; 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp); 2,2'-bipyridyl; 1,2-bis(diphenyl-

phosphino)ethane]. To investigate the strength and nature of the donor–acceptor interactions in these complexes, the crystal structure of [Hg(Cl₂C=CCl)₂].tmp has been determined.

A crystal 0.33 × 0.36 × 0.16 mm was mounted with *b* coincident with the rotation (*ω*) axis of a Stöe Stadi 2 two-circle diffractometer. With monochromated Mo *K*_α radiation and the background-*ω* scan-background technique, 6154 unique reflections were measured of which 4158 had *I* > 3σ(*I*) and were considered to be observed. [The net intensity *I* = *T* – *B*, where *T* = scan count, *B* = mean background count over the scan width; σ(*I*) = (*T* + *Bc*/2*t*)^{1/2}, where *c* = scan time, *t* = time for background measurements at each end of the scan.] Corrections for Lorentz, polarization and absorption effects were made. The Hg atom position was determined from a Patterson function and the remaining atoms were located from successive electron-density maps. H atoms were included in calculated positions (C–H = 1.08 Å). Common isotropic temperature factors were applied to methyl and phenyl H atoms and refined to final values of *U* = 0.233 (40) and 0.068 (15) Å² respectively. Scattering factors were calculated with an analytical approximation (*International Tables for X-ray Crystallography*, 1974) and the weighting scheme was *w* = 1.0000 [σ²(*F*_o) + 0.0075(*F*_o)²]. Full-matrix refinement with anisotropic temperature factors for all non-H