

Structure of Potassium Dichloro(ethylenediaminetetraacetato)ruthenate(III)

BY M. M. TAQUI KHAN, M. M. BHADHHADE, K. VENKATASUBRAMANIAN AND M. R. H. SIDDIQUI

*Discipline of Coordination Chemistry and Homogeneous Catalysis,
Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, India*

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Abstract. (I) $K[Ru(C_{10}H_{14}N_2O_8)Cl_2]$, $M_r = 501$, monoclinic, $P2_1/n$, $a = 10.4470$ (6), $b = 13.947$ (2), $c = 11.296$ (3) Å, $\beta = 106.10$ (1)°, $V = 1581$ (1) Å³, $Z = 4$, $D_x = 2.097$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 16.13$ cm⁻¹, $F(000) = 996$, $T = 295$ (2) K, final $R = 0.031$ ($wR = 0.030$) for 4291 unique observed reflections. In the octahedral coordination group around Ru^{III} there are two N and two O atoms of the ligand and two chlorides *trans* to the N atoms; two —CH₂COOH groups of the ligand are uncomplexed. Ru—Cl distances are 2.3447 (4) and 2.3896 (5) Å, the maximum being somewhat longer than typically observed values. The structure of (I) exhibits disorder: the carboxylate group of one free arm takes up two conformations. The crystal structure is stabilized by interactions between K⁺ and the complex anion and a network of hydrogen bonding (O—H...O) between free carboxylate and chelate ring O atoms.

Introduction. A large number of X-ray crystal structures of metal–edta complexes, including those with Fe (Hamor, Hamor & Hoard, 1964; Mizuta, Yamamoto, Miyoshi & Kushi, 1990) and Os (Saito, Uehiro, Ebina, Iwamoto, Ouchi & Yoshino, 1979), have been reported; only recently have ruthenium(III)–edta complexes been reported (Taqui Khan, Venkatasubramanian, Bhadhbhade, Siddiqui, Bajaj & Shirin, 1990; Vilaplana-Serrano, Basallote, Ruiz-Valero, Gutierrez-Puebla & Gonzalez-Vilchez, 1991; Okamoto, Hidaka, Iida, Higa & Kanamori, 1990). These systems, due to their high lability, have long been the subject of kinetic studies of substitution reactions (Matsubara & Creutz, 1979; Bajaj & van Eldik, 1988; Taqui Khan, Bajaj, Shirin & Venkatasubramanian, 1992). In our laboratory, these have also been shown to be catalytically active in homogeneous catalytic reactions (Taqui Khan, Siddiqui, Hussain & Moiz, 1986; Taqui Khan, Halligudi & Abdi, 1988; Taqui Khan, Samad & Siddiqui, 1989). In most of these, an intermediate with two vacant sites for binding of a substrate and a reactant molecule is proposed (Taqui Khan, Shukla & Prakash Rao, 1989); the molecular geometry of (I) is relevant to the stereochemistry of di-substitutions.

Experimental. $K[Ru(Hedta)Cl] \cdot 2H_2O$ was synthesized by the procedure of Diamantis & Dubarawski (1981), treated with concentrated HCl, and the solution allowed to evaporate slowly. Enraf–Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Crystal $\sim 0.30 \times 0.30 \times 0.13$ mm, unit-cell dimensions by least-squares refinement from 25 reflections with $20 \leq 2\theta \leq 32^\circ$; ω - 2θ scan, three intensity control (every 1 h) and three orientation control reflections (after every 200 scans) remained constant within experimental error throughout the data collection, $2\theta \leq 60^\circ$ ($h = 0 \rightarrow 14$, $k = 0 \rightarrow 19$, $l = -15 \rightarrow 15$), an empirical absorption correction (North, Phillips & Mathews, 1968) based on a series of ψ scans was applied (max. and min. transmission factors 0.93 and 1.00); 4623 reflections measured, 4291 with $|F_o| > 3\sigma(|F_o|)$ used for structure solution by heavy-atom method and refinement. One uncomplexed CH₂COOH group appeared to be disordered: its two conformations differ by rotation about C5—C6 and N1—C5 and have one oxygen site (O13) in common; there are two distinct sites O141 and O142, with site occupancies 0.70 and 0.30 for the second oxygen, but separate sites are not resolved for C5 and C6.

Most of the H atoms were located in a difference map. Positional parameters and anisotropic thermal parameters of non-H atoms, but with the disordered oxygen O141, O142 isotropic, were refined by full-matrix least squares (on F) using unit weights. H atoms not refined; scattering factors (including f' , f'' terms for Ru and Cl) were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were carried out on a PDP-11/73 computer using SDP software (B. A. Frenz & Associates, Inc., 1985). Atomic coordinates are listed in Table 1 and selected bond lengths and angles in Table 2.* $R = 0.031$ ($wR = 0.030$), $S = 0.78$, $\Delta/\sigma < 0.03$, 217

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54892 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0077]

Table 1. Atomic positional parameters of non-hydrogen atoms with their isotropic equivalent temperature factors

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Ru1	0.21889 (1)	0.74241 (1)	0.06101 (1)	1.293 (1)
K	0.88269 (5)	0.64591 (4)	0.12544 (5)	2.730 (7)
Cl21	0.11669 (5)	0.58970 (3)	0.00566 (5)	2.373 (7)
Cl22	0.01141 (4)	0.81916 (4)	0.00626 (4)	2.121 (6)
O13	0.4696 (3)	1.0595 (2)	0.1613 (4)	4.34 (5)
O15	0.2036 (2)	0.8062 (3)	0.4032 (2)	4.18 (5)
O16	0.2068 (2)	0.7288 (2)	0.2358 (1)	2.61 (3)
O17	0.3290 (2)	0.6834 (1)	-0.2443 (1)	2.50 (2)
O18	0.2435 (1)	0.7580 (1)	-0.1102 (1)	1.71 (2)
O19	0.6532 (2)	0.5655 (1)	0.1644 (2)	2.40 (2)
O20	0.5494 (2)	0.4768 (1)	0.2761 (2)	2.71 (2)
O141	0.2872 (3)	1.1138 (2)	0.0224 (3)	2.95 (4)*
O142	0.2611 (7)	1.0868 (5)	0.1313 (7)	2.77 (8)*
N1	0.3219 (1)	0.8678 (1)	0.1388 (1)	1.61 (2)
N4	0.4120 (1)	0.6841 (1)	0.0879 (1)	1.33 (2)
C2	0.4639 (2)	0.8378 (1)	0.1955 (2)	1.96 (2)
C3	0.5056 (2)	0.7670 (1)	0.1123 (2)	1.70 (2)
C5	0.3075 (2)	0.9445 (1)	0.0451 (2)	1.99 (2)
C6	0.3616 (2)	1.0417 (2)	0.0960 (3)	3.08 (4)
C7	0.2600 (2)	0.8954 (2)	0.2395 (2)	2.62 (3)
C8	0.2219 (2)	0.8061 (3)	0.2996 (2)	2.92 (4)
C9	0.4098 (2)	0.6383 (1)	-0.0316 (1)	1.46 (2)
C10	0.3221 (2)	0.6965 (1)	-0.1375 (1)	1.63 (2)
C11	0.4384 (2)	0.6139 (1)	0.1901 (2)	1.78 (2)
C12	0.5606 (2)	0.5514 (1)	0.2080 (2)	1.74 (2)

* Refined isotropically.

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$)

Ru1—Cl21	2.3896 (5)	K—Cl21	3.207 (1)
Ru1—Cl22	2.3447 (4)	K—Cl22	3.239 (1)
Ru1—O16	2.025 (2)	K—O13	2.756 (3)
Ru1—O18	2.036 (1)	K—O15	2.769 (2)
Ru1—N1	2.115 (1)	K—O17	2.937 (2)
Ru1—N4	2.121 (1)	K—O19	2.793 (2)
Cl21—Ru1—Cl22	91.41 (2)	O16—Ru1—O18	176.36 (7)
Cl21—Ru1—O16	91.57 (7)	O16—Ru1—N1	80.43 (8)
Cl21—Ru1—O18	90.66 (4)	O16—Ru1—N4	97.97 (6)
Cl21—Ru1—N1	170.66 (4)	O18—Ru1—N1	97.09 (6)
Cl21—Ru1—N4	91.97 (4)	O18—Ru1—N4	79.08 (5)
Cl22—Ru1—O16	89.83 (5)	N1—Ru1—N4	84.44 (5)
Cl22—Ru1—O18	92.99 (4)		
Cl22—Ru1—N1	93.38 (4)		
Cl22—Ru1—N4	171.41 (5)		

H-bonding contacts

O15...O141	2.808 (6)
O16...O142	2.455 (8)
O17...O20	2.646 (3)

parameters refined, reflections/number of parameters = 20, variation of $\Delta\rho$ in final difference map between -0.7 and $+0.7 e \text{\AA}^{-3}$, except some peaks $< 1.5 e \text{\AA}^{-3}$ near the disordered carboxylate and O15.

Discussion. The molecule is shown in Fig. 1. The ligand edta is tetradentate with two $-\text{CH}_2\text{COOH}$ arms uncomplexed; the two chlorides are *cis* to each other and *trans* to the two ethylenediamine N atoms;

Ru^{III} is six-coordinate. The positions of the chlorides in the complex indicate the preferred substitution sites on the parent molecule; the two P atoms of the dppm ligand were also observed to be *trans* to the N atoms of edta in the crystal structure of $[\text{Ru}(\text{H}_2\text{edta})\text{-(dppm)}]\text{.dmsO.H}_2\text{O}$ (Taqui Khan, Shirin, Venkatasubramanian & Bhadbhade, 1992) (dppm = bis(diphenylphosphino)methane; dmsO = dimethyl sulfoxide). As seen from Fig. 1 and Table 2, the molecule has approximate twofold symmetry. The Ru^{III} coordination can strictly be described as a rhombic compressed octahedron with three sets of bond distances: Ru—Cl (longest), Ru—O (shortest) and Ru—N (intermediate) (see Table 2); the bond angles deviate from the ideal octahedral values mainly because of the 'bites' taken by the five-membered chelate rings. The Ru—Cl distances are unequal [Ru1—Cl21 = 2.3896 (5), Ru1—Cl22 = 2.3477 (4) \AA]. The Ru—N distances are more nearly equal, despite the greater difference between the *trans* metal to chloride bonds.

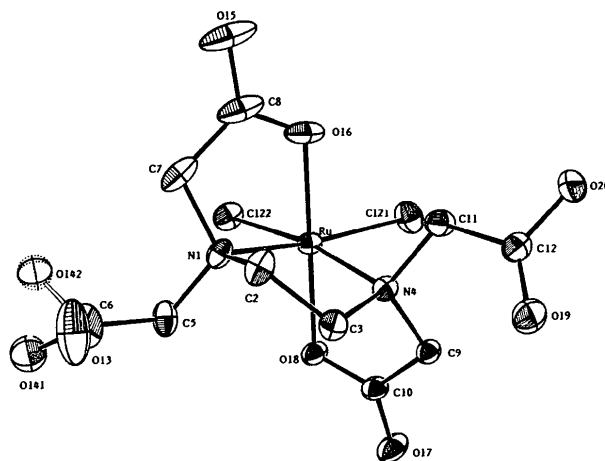


Fig. 1. ORTEP view of the complex (Johnson, 1976).

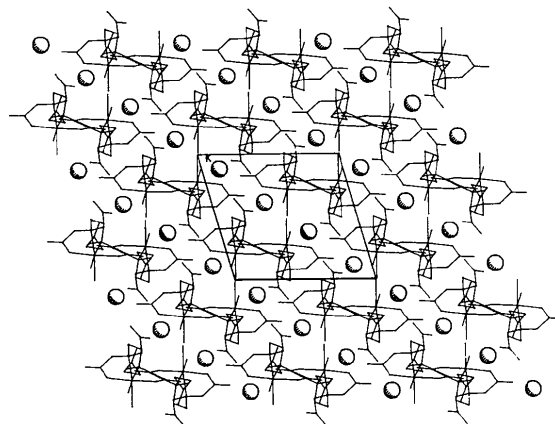


Fig. 2. Packing of molecules in the unit cell; viewed down *b*.

The potassium ion is coordinated in a very distorted octahedron by four O atoms and two chloride ions. Fig. 2 shows the alternating layers of cations (K⁺) and complex anions parallel to the diagonal (101).

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Structure of Tetraethylammonium Nonacarbonyl- μ_3 -{[dichloro(undecacarbonyl-cobaltio)silyl]oxymethylidyne}-tricobaltate, [Et₄N][Cl₂SiCo₇(CO)₂₁]

BY GLEN C. BARRIS

Department of Scientific and Industrial Research, Gracefield, Lower Hutt, New Zealand

AND KENNETH M. MACKAY AND BRIAN K. NICHOLSON*

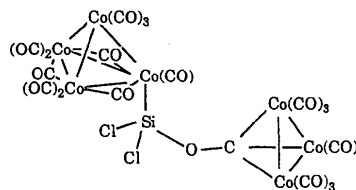
School of Science and Technology, University of Waikato, Hamilton, New Zealand

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Abstract. C₂₉H₂₀Cl₂Co₇NO₂₁Si, *M_r* = 1230.0, monoclinic, *P*2₁/*c*, *a* = 9.110 (4), *b* = 22.472 (9), *c* = 21.01 (1) Å, β = 95.28 (4)°, *V* = 4283 (3) Å³, *Z* = 4, *D_x* = 1.91 g cm⁻³, λ (Mo *K*α) = 0.7107 Å, μ = 29 cm⁻¹, *F*(000) = 2424, *T* = 148 K, *R* = 0.0555 for 2626 [*I* > 3σ(*I*)] reflections. The Si atom is bonded to two Cl atoms [Si—Cl (av.) = 2.094 (6) Å, Cl—Si—Cl = 101.7 (2)°], to a Co₄(CO)₁₁ moiety [Si—Co = 2.209 (5) Å, Co—Si—Cl (av.) = 118.0 (3)°], and to the O atom of a μ_3 -CO group which bridges a Co₃(CO)₉ unit [Si—O = 1.67 (1), O—C = 1.32 (2) Å, O—Si—Cl (av.) = 102.9 (4), O—Si—Co = 111.1 (4)°].

Introduction. The reaction of Si[Co₂(CO)₇]₂ with [Et₄N][Co(CO)₄] proceeds to give the mixed salt [Et₄N]₃[SiCo₉(CO)₂₁][Co(CO)₄] in high yields

(Mackay, Nicholson & Sims, 1984; Barris, 1986). On further investigation of this reaction, [Et₄N][Cl₂SiCo₇(CO)₂₁] (I) has now been isolated as a minor component of the product mixture by extraction into diethyl ether, and has been characterized by X-ray crystallography. The Cl atoms in [Et₄N][Cl₂SiCo₇(CO)₂₁] appear to be derived from residual [Et₄N]Cl carried over from the preparation of the [Et₄N][Co(CO)₄] reagent.



(I)

* Author to whom correspondence should be addressed.