Fig. 4. Projection parallel to the two different chains into the *ab* plane. The two different trigonally coordinated Cu^I ions in the Cl—Cu—Cl···Cu···Cl chains and the square-planar platinum-(II,IV) complex units are shown.

types of trigonal bipyramids [type 1: Cu(1)—Cl(2) apical = 3·10 (1) Å, Cu(1)—Cl(3) equatorial = 2·291 (9) Å; type 2: Cu(2)—Cl(2) apical = 2·16 (1) Å, Cu(2)—Cl(4) equatorial = 3·48 (1) Å] sharing their apices. The repeating distance in the Cu system is 10·522 (7) Å, the *c* axis of the unit cell. As the Pt—Pt distance is exceedingly short for this class of compounds, it may be argued that the distances along the Cu—halogen chains are responsible for the short *c*-axis

length, and that the Pt complex units arrange themselves accordingly. The arrangement of the parallel chains is shown in Fig. 4.

Another example of Cu—*X*—Cu chains running parallel to the Pt—*X*—Pt chains was reported recently (Keller, Martin & Traeger, 1978).

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The Crystal Structures of [1,2-Bis(diphenylphosphino)ethane]trichloro-(η-cyclopentadienyl)niobium(IV) Bistoluene Solvate and μ-Oxo-bis[aquatrichloro-(η-methylcyclopentadienyl)niobium(V)]

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Abstract

The structures of two new halo monocyclopentadienyl derivatives of Nb have been determined. They crystal-lize in the triclinic system, space group $P\bar{1}$, $a = 9·112$ (3), $b = 11·996$ (3), $c = 17·113$ (5) Å, $\alpha = 70·40$ (2), $\beta = 87·41$ (2), $\gamma = 80·32$ (2)°, $Z = 2$, for $C_{31}H_{29}Cl_3NbP_2.2C_7H_8$, $[Nb(C_5H_5)(C_{26}H_{24}P_2)Cl_3].2C_7H_8$ (I), and $a = 7·352$ (1), $b = 11·094$ (2), $c = 12·973$ (1) Å, $\alpha = 75·12$ (1), $\beta = 75·50$ (1), $\gamma = 86·28$ (1)°, $Z = 2$, for $C_{12}H_{18}Cl_6Nb_2O_3$, $[Nb_2(C_6H_7)_2Cl_6(H_2O)_2O]$ (II). The structures were refined to $R = 0·057$ (I) and $R = 0·045$ (II). Both complexes contain *quasi*-octahedrally coordinated Nb atoms with a cyclo-pentadienyl ring at one apex, η^5-bonded to Nb, three Cl atoms at three of the apices of the equatorial plane and the remaining sites occupied by P atoms of a chelating

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diphosphine ligand in (I) and a water molecule and an O atom in (II). (II) is a dimer, the O atom bridging two Nb atoms.

Introduction

Since the halo monocyclopentadienyl derivatives of Nb and Ta can be the precursors to a wide range of new compounds, attempts have been made to open up this highly promising chemistry (Burt, Chatt, Leigh, Teuben & Westerhof, 1977; Bunker, De Cian & Green, 1977). Here we describe the crystal structures of two of these new compounds: the violet Nb^{IV} complex (η-$C_5H_5)NbCl_3[(C_6H_5)_2(PCH_2)_2(C_6H_5)_2].2C_6H_5CH_3$ (I) and the orange Nb^V complex $[(\eta$-$C_5H_4CH_3)NbCl_3$-$(H_2O)]_2O$ (II). The crystals were provided by Dr M. L. H. Green and Dr A. De Cian. This work has been the subject of a preliminary publication (Daran, Prout, De Cian, Green & Siganporia, 1977) in which (II) was incorrectly described as a hydroxyl derivative.

Experimental

After survey photography by Weissenberg and precession techniques, a selected crystal of each compound was set up on an Enraf–Nonius CAD-4F diffractometer with Mo $K\alpha$ radiation. In each case 25 of the strongest reflections in the range $30 < 2\theta < 32°$ were used to obtain accurate cell dimensions and orientation matrices. The intensity of each independent reflection with $\sin \theta < 0.7$ was measured by an $\omega/2\theta$ scan. Scan ranges of $(0.8 + 0.35 \tan \theta)°$ and $(1.0 + 0.35 \tan \theta)°$ were employed for (I) and (II) respectively. Reflections with $\sigma(I)/I < 0.3$ were declared unobserved and excluded from subsequent calculations. The data were corrected for Lorentz and polarization effects and the effect of the graphite-crystal monochromator. In view of the low absorption coefficients, only empirical absorption corrections (North, Phillips & Mathews, 1968) were applied.

Crystal data

Compound (I): $(\eta$-$C_5H_5)NbCl_3[(C_6H_5)_2(PCH_2)_2$-$(C_6H_5)_2].2C_6H_5CH_3$, violet crystal, $M_r = 1276$, triclinic, space group $P\bar{1}$, $a = 9.112$ (3), $b = 11.996$ (3), $c = 17.113$ (5) Å, $\alpha = 70.40$ (2), $\beta = 87.41$ (2), $\gamma = 80.32$ (2)°, $U = 1737$ Å³, $Z = 2$, $D_m = 2.40$, $D_x = 2.44$ Mg m⁻³, $\mu = 0.685$ mm⁻¹, 6188 independent reflections.

Compound (II): $[(\eta$-$C_5H_4CH_3)NbCl_3(H_2O)]_2O$, redbrown crystal, $M_r = 608$, triclinic, space group $P\bar{1}$, $a = 7.352$ (1), $b = 11.094$ (2), $c = 12.973$ (1) Å, $\alpha = 75.12$ (1), $\beta = 75.50$ (1), $\gamma = 86.28$ (1)°, $U = 990$ Å³, $Z = 2$, $D_x = 2.03$ Mg m⁻³, $\mu = 1.933$ mm⁻¹, 4974 independent reflections.

Structure solution and refinement

Both structures were solved by heavy-atom techniques. Nb and Cl were found from unsharpened Patterson functions. The subsequent F_o syntheses indicated the C, P and O atoms. In (I), two molecules of toluene of crystallization were found on a difference synthesis. Each of these molecules was statistically distributed between two sites related by an inversion centre, one at $0\frac{1}{2}\frac{1}{2}$ and the other at $\frac{1}{2}\frac{1}{2}0$. The electron density at the toluene molecule $C(61)$–$C(65)$ is shown in Fig. 1. Also H atoms attached to the cyclopentadienyl and phenyl rings, and those attached to the O atom of the water molecule in (II) were found in the difference map.

Refinement was by least squares with a large-block approximation to the normal matrix. The derivatives of the positional parameters and the U_{ii} and U_{ij} components of the anisotropic temperature factors of the complex were contained in three distinct blocks, and in (I) those of the positional and anisotropic temperature parameters of the disordered toluene molecules were in a separate block. In (I) both toluene molecules were severely constrained to chemically reasonable dimensions by the method of Waser (1963) implemented by Rollett (1969). The refinements converged at $R = 0.057$ (I) and $R = 0.045$ (II). In the last stages of the refinements, each reflection was assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r(X)$ where n is the number of coefficients, A_r, for a Chebyshev series, for which X is F_o/F_o(max.) (Rollett, 1965). Three coefficients, A_r, were used with values 7.70, 10.77, 4.05 for (I) and 50.46, 67.38, 19.53 for (II). The final R_w values were 0.052 and 0.058 respectively. All calculations were performed on the Oxford University ICL 1906A computer with the Oxford CRYSTALS package (Carruthers, 1975). Scattering factors and corrections for the real part of the anomalous dispersion were taken from International Tables for X-ray Crystallography (1974).
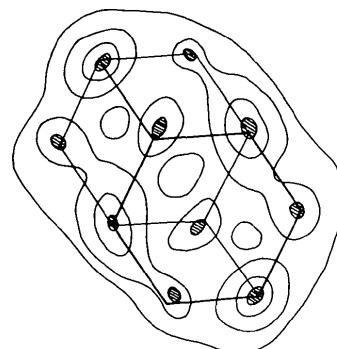

Fig. 1. Section of the difference electron density through the best plane of $C(61)$–$C(65)$. The disordered model is shown fitted to the electron density.

Results and discussion

Atomic coordinates* are given in Tables 1 and 2, bond lengths and angles with e.s.d.'s calculated from the block approximation to the normal variance–covariance matrix in Tables 3 and 4, and details of important molecular planes in Table 5.

(I), formally a complex of Nb^{IV}, is shown in Fig. 2 projected on to the Nb, P(1), P(2) plane. The Nb atom is at the centre of a distorted coordination octahedron of three Cl atoms, a chelating diphosphine ligand and an η-cyclopentadienyl residue. The overall stereochemistry resembles that of the oxotrichloro complexes such as $NbOCl_3(NCCH_3)_2$ (Chavant, Daran, Jeannin,

* Lists of structure factors, anisotropic thermal parameters, lengths and angles in the phenyl rings for (I) and angles in the methylcyclopentadienyl rings for (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34684 (87 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Constant & Morancho, 1975), and $[NbOCl_3(C_4H_3\text{-}SCOCHCOCF_3)]^-$ (Daran, Jeannin, Guerchais & Kergoat, 1979) with the cyclopentadienyl group in place of the oxo atom. The Nb atom lies 0·622 Å above the plane of the four equatorial Cl(1), Cl(2), Cl(3) and P(1) atoms (Table 5) towards the η-C_5H_5 residue. The Nb—Cl lengths of 2·481, 2·463 and 2·475 Å are in good agreement with the 2·47 and 2·46 Å found in the Nb^{IV} complex $(\eta\text{-}C_5H_5)_2NbCl_2$ (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). Cl—Nb—Cl and Cl—Nb—P(1) angles range from 74·98 to 92·48°. P(1), P(2), C(1) and C(2) form a five-membered chelate ring at the Nb with a P—Nb—P angle of 74·01 (5)°. C(1) and C(2) lie one on each side of the Nb, P(1), P(2) plane, 0·697 and −0·130 Å away from it. Covalent radii arguments (Pauling, 1960) suggest that the Nb—P distance should be of the same magnitude as Mo—P. However, the two independent Nb—P lengths of 2·678 and 2·787 Å are about 0·2 Å longer than the Mo—P distance of 2·50 Å in $[(\eta\text{-}C_5H_5)(\eta^4\text{-}C_6H_8)Mo(diphos)]\text{-}PF_6.SO_2$ (Prout & Daran, 1977) and 2·48 Å in $[(\eta\text{-}$

Table 1. *Compound* (I): $(\eta\text{-}C_5H_5)NbCl_3[(C_6H_5)_2(PCH_2)_2(C_6H_5)_2].2C_6H_5CH_3$, *fractional atomic coordinates, with e.s.d.'s in parentheses*

	x	y	z		x	y	z
Nb(1)	0·03043 (4)	0·11576 (3)	0·27114 (2)	H(12)	0·1052	0·4425	0·0919
Cl(1)	−0·0422 (1)	−0·0577 (1)	0·24326 (7)	H(13)	−0·0117	0·6447	0·0511
Cl(2)	0·1756 (1)	−0·0355 (1)	0·38854 (6)	H(14)	−0·0567	0·7469	0·1534
Cl(3)	0·0022 (1)	0·2258 (1)	0·12038 (6)	H(15)	0·0071	0·6627	0·2971
P(1)	0·2121 (1)	0·27524 (9)	0·25656 (6)	H(16)	0·1292	0·4538	0·3450
P(2)	0·2915 (1)	0·03414 (9)	0·20181 (6)	H(22)	0·4467	0·3854	0·2813
C(1)	0·3461 (5)	0·2655 (4)	0·1750 (3)	H(23)	0·6106	0·3991	0·3635
C(11)	0·1258 (4)	0·4330 (4)	0·2217 (3)	H(24)	0·5756	0·2347	0·5173
C(21)	0·3317 (5)	0·2624 (4)	0·3434 (3)	H(25)	0·3918	0·1086	0·5427
C(12)	0·0837 (6)	0·4926 (4)	0·1395 (3)	H(26)	0·2343	0·1290	0·4281
C(13)	0·0122 (6)	0·6120 (5)	0·1146 (3)	H(32)	0·2065	−0·2076	0·2651
C(14)	−0·0107 (6)	0·6716 (4)	0·1721 (3)	H(33)	0·3567	−0·4155	0·3236
C(15)	0·0289 (6)	0·6129 (4)	0·2536 (3)	H(34)	0·6154	−0·4368	0·3422
C(16)	0·0979 (5)	0·4940 (4)	0·2786 (3)	H(35)	0·7530	−0·2460	0·3029
C(22)	0·4402 (5)	0·3345 (4)	0·3318 (3)	H(36)	0·6002	−0·0542	0·2482
C(23)	0·5325 (5)	0·3242 (5)	0·3970 (4)	H(42)	0·3998	0·1736	0·0496
C(24)	0·5190 (6)	0·2426 (5)	0·4733 (4)	H(43)	0·3664	0·1508	−0·0897
C(25)	0·4105 (8)	0·1718 (6)	0·4861 (4)	H(44)	0·2463	0·0157	−0·1114
C(26)	0·3162 (7)	0·1817 (5)	0·4213 (3)	H(45)	0·1434	−0·1132	−0·0111
C(2)	0·4244 (4)	0·1349 (4)	0·1982 (3)	H(46)	0·1695	−0·0990	0·1305
C(31)	0·2804 (4)	0·0340 (4)	0·0956 (2)	H(52)	−0·2823	0·2003	0·2171
C(41)	0·4010 (5)	−0·1137 (4)	0·2522 (3)	H(53)	−0·1457	0·3525	0·2328
C(32)	0·3449 (6)	0·1140 (5)	0·0295 (3)	H(54)	−0·0204	0·2853	0·3737
C(33)	0·3338 (7)	0·1100 (6)	−0·0500 (3)	H(55)	−0·1004	0·0846	0·4329
C(34)	0·2604 (6)	0·0271 (6)	−0·0642 (3)	H(56)	−0·2291	0·0192	0·3705
C(35)	0·1960 (6)	−0·0502 (6)	−0·0002 (4)	C(61)	−0·1120 (8)	0·5780 (7)	0·4849 (3)
C(36)	0·2082 (6)	−0·0490 (6)	0·0809 (3)	C(62)	−0·023 (2)	0·6714 (8)	0·4632 (5)
C(42)	0·5534 (5)	−0·1282 (4)	0·2648 (3)	C(63)	0·134 (1)	0·6373 (9)	0·4682 (4)
C(43)	0·6389 (6)	−0·2412 (5)	0·2963 (4)	C(64)	0·201 (1)	0·515 (1)	0·4942 (6)
C(44)	0·5723 (7)	−0·3401 (5)	0·3164 (5)	C(65)	−0·048 (1)	0·4545 (8)	0·5110 (5)
C(45)	0·4197 (7)	−0·3279 (5)	0·3052 (5)	C(71)	0·3886 (8)	0·5764 (6)	−0·0034 (6)
C(46)	0·3341 (6)	−0·2156 (5)	0·2747 (4)	C(72)	0·454 (2)	0·6109 (9)	0·0574 (7)
C(3)	−0·2265 (5)	0·1938 (5)	0·2646 (3)	C(73)	0·598 (1)	0·553 (1)	0·0889 (5)
C(4)	−0·1514 (5)	0·2832 (4)	0·2714 (3)	C(74)	0·675 (1)	0·460 (1)	0·0617 (7)
C(5)	−0·0842 (5)	0·2417 (5)	0·3498 (3)	C(75)	0·466 (1)	0·4815 (9)	−0·0305 (6)
C(6)	−0·1205 (6)	0·1283 (6)	0·3918 (3)				
C(7)	−0·2100 (6)	0·0986 (5)	0·3383 (4)				

Table 2. *Compound* (II): [(η-C₅H₄CH₃)NbCl₃-(H₂O)]₂O, *fractional atomic coordinates, with e.s.d.'s in parentheses*

Table 2. *Compound* (II): $[(\eta\text{-}C_5H_4CH_3)NbCl_3\text{-}(H_2O)]_2O$, *fractional atomic coordinates, with e.s.d.'s in parentheses*

	x	y	z
Nb(1)	0·12591 (4)	0·22847 (3)	0·09291 (2)
Nb(2)	0·14463 (4)	0·27255 (3)	0·37238 (2)
O(1)	0·1543 (3)	0·2495 (2)	0·2289 (2)
Cl(11)	−0·1467 (1)	0·0882 (1)	0·19329 (9)
Cl(12)	0·2863 (2)	0·42842 (9)	0·00349 (9)
Cl(13)	−0·0275 (2)	0·2727 (1)	−0·05973 (9)
Cl(21)	−0·1144 (2)	0·4247 (1)	0·3501 (1)
Cl(22)	0·2927 (2)	0·0670 (1)	0·4153 (1)
Cl(23)	0·0013 (2)	0·2364 (2)	0·56764 (9)
O(11)	−0·1006 (4)	0·3580 (3)	0·1352 (2)
O(21)	−0·0953 (5)	0·1512 (3)	0·4000 (2)
C(11)	0·2511 (7)	0·0197 (4)	0·1164 (5)
C(12)	0·3845 (7)	0·0914 (5)	0·1338 (4)
C(13)	0·4575 (6)	0·1748 (5)	0·0360 (5)
C(14)	0·3749 (7)	0·1559 (4)	−0·0461 (4)
C(15)	0·2458 (7)	0·0592 (4)	0·0070 (5)
C(16)	0·421 (1)	0·2207 (8)	−0·1663 (5)
C(21)	0·2937 (8)	0·4728 (5)	0·2944 (5)
C(22)	0·4183 (7)	0·3915 (5)	0·2521 (4)
C(23)	0·4800 (6)	0·3104 (5)	0·3383 (4)
C(24)	0·3964 (6)	0·3475 (5)	0·4362 (4)
C(25)	0·2771 (7)	0·4480 (5)	0·4071 (5)
C(26)	0·437 (1)	0·2937 (9)	0·5461 (5)
H(1)	−0·08 (1)	0·380 (7)	0·182 (3)
H(2)	−0·07 (1)	0·109 (7)	0·347 (4)
H(3)	0·87 (1)	0·419 (7)	0·073 (6)
H(4)	0·848 (7)	0·107 (7)	0·457 (6)
H(11)	0·18 (1)	−0·054 (7)	0·183 (6)
H(12)	0·40 (1)	0·089 (7)	0·200 (6)
H(13)	0·54 (1)	0·236 (7)	0·027 (6)
H(15)	0·170 (8)	0·020 (7)	−0·004 (6)
H(21)	0·24 (1)	0·513 (7)	0·269 (6)
H(22)	0·45 (1)	0·383 (7)	0·176 (6)
H(23)	0·56 (1)	0·271 (7)	0·339 (6)
H(25)	0·18 (1)	0·483 (7)	0·452 (6)

Table 3. *Compound* (I): $(\eta\text{-}C_5H_5)NbCl_3[(C_6H_5)_2(PCH_2)_2(C_6H_5)_2].2C_6H_5CH_3$, *interatomic distances* (Å) *and bond angles* (°)

Nb—Cl(1)	2·481 (1)	Cl(1)—Nb—Cl(2)	85·50 (4)
Nb—Cl(2)	2·463 (1)	Cl(1)—Nb—Cl(3)	87·47 (4)
Nb—Cl(3)	2·475 (1)	Cl(1)—Nb—P(1)	152·84 (4)
Nb—P(1)	2·678 (1)	Cl(1)—Nb—P(2)	79·38 (4)
Nb—P(2)	2·787 (1)	Cl(2)—Nb—Cl(3)	149·70 (4)
Nb—C(3)	2·364 (4)	Cl(2)—Nb—P(1)	92·48 (4)
Nb—C(4)	2·380 (4)	Cl(2)—Nb—P(2)	74·76 (4)
Nb—C(5)	2·427 (4)	Cl(3)—Nb—P(1)	80·69 (4)
Nb—C(6)	2·461 (5)	Cl(3)—Nb—P(2)	74·98 (3)
Nb—C(7)	2·435 (5)	P(1)—Nb—P(2)	74·01 (5)
		Nb—P(1)—C(1)	107·8 (1)
P(1)—C(1)	1·833 (4)	Nb—P(1)—C(11)	116·3 (1)
P(1)—C(11)	1·828 (4)	Nb—P(1)—C(21)	120·8 (1)
P(1)—C(21)	1·833 (4)	C(1)—P(1)—C(11)	103·6 (2)
C(1)—C(2)	1·535 (6)	C(1)—P(1)—C(21)	103·0 (2)
P(2)—C(2)	1·835 (4)	C(11)—P(1)—C(21)	103·4 (2)
P(2)—C(31)	1·825 (4)	Nb—P(2)—C(2)	107·3 (1)
P(2)—C(41)	1·828 (4)	Nb—P(2)—C(31)	117·4 (4)
		Nb—P(2)—C(41)	121·7 (1)
C(3)—C(4)	1·403 (7)	C(2)—P(2)—C(31)	105·1 (2)
C(4)—C(5)	1·395 (7)	C(2)—P(2)—C(41)	102·3 (2)
C(5)—C(6)	1·397 (8)	C(31)—P(2)—C(41)	101·1 (2)
C(6)—C(7)	1·418 (9)	P(1)—C(1)—C(2)	107·8 (3)
C(7)—C(3)	1·383 (8)	P(1)—C(11)—C(12)	121·0 (3)
		P(1)—C(11)—C(16)	119·9 (3)
		P(1)—C(21)—C(22)	120·3 (3)
C(3)—C(4)—C(5)	108·0 (5)	P(1)—C(21)—C(26)	121·2 (3)
C(4)—C(5)—C(6)	107·7 (5)	P(2)—C(2)—C(1)	111·1 (3)
C(5)—C(6)—C(7)	108·3 (5)	P(2)—C(31)—C(32)	122·0 (3)
C(6)—C(7)—C(3)	107·1 (5)	P(2)—C(31)—C(36)	118·7 (4)
C(7)—C(3)—C(4)	108·9 (5)	P(2)—C(41)—C(42)	121·4 (3)
		P(2)—C(41)—C(46)	120·3 (4)

C₅H₅)(diphos)Mo(CO)Cl] (Cross & Fenn, 1970). Moreover the bond Nb—P(2) *trans* to the cyclopentadienyl ring is much longer than Nb—P(1). The close Cl···P non-bonding contacts (Table 6), especially the Cl···P(2) distances of 3·37, 3·20 and 3·21 Å, are less than the expected van der Waals contact of 3·6 Å (Bondi, 1964). This suggests that the lengthening of the Nb—P bonds may, in part, result from steric repulsions. The bond distances and angles in the diphenylphosphine ligand are essentially the same as those reported by Churchill & O'Brien (1970).

The η-cyclopentadienyl ring is planar with C—C bonds in the range 1·383–1·418 Å (mean 1·40 Å) and C—C—C angles in the range 107·1–108·9° (mean 108·0°). The length of the normal to the mean plane of the ring at the Nb atom is 2·092 Å, in good agreement with the values observed in (η-C₅H₅)₂NbCl₂, 2·09 Å, {[(η-C₅H₅)₂NbCl]₂O}(BF₄)₂, 2·10 Å, (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974) and {[(η-C₅H₅)₂Nb(SCH₃)₂]₂Ni}(BF₄)₂, 2·10 Å, (Prout, Critchley & Rees, 1974). This normal meets the ring

Table 4. *Compound* (II): $[(\eta\text{-}C_5H_4CH_3)NbCl_3(H_2O)]_2O$, *interatomic distances* (Å) *and angles* (°)

Nb(1)—Cl(11)	2·488 (1)	Nb(2)—Cl(21)	2·483 (1)
Nb(1)—Cl(12)	2·447 (1)	Nb(2)—Cl(22)	2·454 (1)
Nb(1)—Cl(13)	2·446 (1)	Nb(2)—Cl(23)	2·426 (1)
Nb(1)—O(11)	2·186 (3)	Nb(2)—O(21)	2·191 (3)
Nb(1)—O(1)	1·901 (2)	Nb(2)—O(1)	1·926 (2)
Nb(1)—C(11)	2·409 (4)	Nb(2)—C(21)	2·402 (5)
Nb(1)—C(12)	2·434 (4)	Nb(2)—C(22)	2·436 (4)
Nb(1)—C(13)	2·444 (4)	Nb(2)—C(23)	2·439 (4)
Nb(1)—C(14)	2·481 (4)	Nb(2)—C(24)	2·475 (4)
Nb(1)—C(15)	2·433 (4)	Nb(2)—C(25)	2·421 (4)
C(11)—C(12)	1·396 (9)	C(21)—C(22)	1·360 (9)
C(12)—C(13)	1·369 (8)	C(22)—C(23)	1·396 (8)
C(13)—C(14)	1·415 (8)	C(23)—C(24)	1·418 (7)
C(14)—C(15)	1·397 (7)	C(24)—C(25)	1·406 (8)
C(15)—C(11)	1·383 (8)	C(25)—C(21)	1·392 (9)
C(14)—C(16)	1·501 (8)	C(24)—C(26)	1·494 (8)
Cl(11)—Nb(1)—Cl(12)	155·97 (4)	Cl(21)—Nb(2)—Cl(22)	157·13 (5)
Cl(11)—Nb(1)—Cl(13)	84·81 (4)	Cl(21)—Nb(2)—Cl(23)	84·97 (5)
Cl(11)—Nb(1)—O(11)	76·8 (1)	Cl(21)—Nb(2)—O(21)	77·6 (1)
Cl(11)—Nb(1)—O(1)	89·75 (7)	Cl(21)—Nb(2)—O(1)	88·74 (8)
Cl(12)—Nb(1)—Cl(13)	86·18 (4)	Cl(22)—Nb(2)—Cl(23)	87·04 (6)
Cl(12)—Nb(1)—O(11)	79·3 (1)	Cl(22)—Nb(2)—O(21)	79·6 (1)
Cl(12)—Nb(1)—O(1)	88·02 (7)	Cl(22)—Nb(2)—O(1)	88·17 (8)
Cl(13)—Nb(1)—O(11)	75·38 (8)	Cl(23)—Nb(2)—O(21)	75·67 (9)
Cl(13)—Nb(1)—O(1)	152·49 (8)	Cl(23)—Nb(2)—O(1)	151·60 (8)
O(11)—Nb(1)—O(1)	77·1 (1)	O(21)—Nb(2)—O(1)	75·9 (1)
Nb(1)—O(1)—Nb(2)	171·8 (1)		

Table 5. Least-squares planes

In the equations, x, y and z represent fractional coordinates with respect to the crystallographic axes. The table gives the displacement (Å) of the specified atom from the plane.

(I) $(\eta$-C$_5$H$_5$)NbCl$_3$[(C$_6$H$_5$)$_2$(PCH$_2$)$_2$(C$_6$H$_5$)$_2$].2C$_6$H$_5$CH$_3$
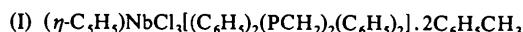
Plane 1: ring C(3) to C(7)

$$-6 \cdot 769x + 5 \cdot 204y + 8 \cdot 392z = 4 \cdot 769$$

C(3)	0·007 (5)	C(6)	−0·002 (6)
C(4)	−0·007 (5)	C(7)	−0·005 (6)
C(5)	0·006 (5)	Nb	−2·092 (7)

Plane 2: P(1), Cl(1), Cl(2) and Cl(3)

$$6 \cdot 762x - 4 \cdot 784y - 9 \cdot 042z = -2 \cdot 180$$

P(1)	−0·023 (1)	Cl(3)	0·026 (1)
Cl(1)	−0·029 (1)	Nb	−0·622 (11)
Cl(2)	0·024 (1)		

Plane 3: Nb, P(1) and P(2)

$$-2 \cdot 966x + 2 \cdot 128y - 13 \cdot 673z = -3 \cdot 551$$

C(1)	0·697 (5)	C(2)	−0·130 (5)

Plane 4: ring C(11) to C(16)

$$8 \cdot 659x + 4 \cdot 801y - 0 \cdot 994z = 2 \cdot 946$$

C(11)	0·002 (4)	C(14)	0·015 (6)
C(12)	0·006 (6)	C(15)	−0·005 (6)
C(13)	−0·016 (6)	C(16)	−0·003 (5)

Plane 5: ring C(21) to C(26)

$$4 \cdot 763x - 8 \cdot 609y - 8 \cdot 162z = -3 \cdot 469$$

C(21)	0·008 (5)	C(24)	0·009 (6)
C(22)	−0·002 (5)	C(25)	−0·003 (7)
C(23)	−0·006 (6)	C(26)	−0·008 (6)

Plane 6: ring C(31) to C(36)

$$6 \cdot 876x - 6 \cdot 037y - 0 \cdot 673z = 1 \cdot 664$$

C(31)	−0·005 (4)	C(34)	0·007 (6)
C(32)	0·001 (5)	C(35)	−0·013 (5)
C(33)	0·001 (6)	C(36)	0·009 (4)

Plane 7: ring C(41) to C(46)

$$-0 \cdot 899x + 4 \cdot 104y + 16 \cdot 925z = 3 \cdot 450$$

C(41)	−0·008 (4)	C(44)	−0·004 (6)
C(42)	0·009 (6)	C(45)	−0·007 (7)
C(43)	0·002 (6)	C(46)	0·015 (6)

(II) [(η-C$_5$H$_4$CH$_3$)NbCl$_3$(H$_2$O)]$_2$O

Plane 1: ring C(11) to C(15)

$$4 \cdot 633x - 7 \cdot 765y - 3 \cdot 042z = 0 \cdot 659$$

C(11)	−0·002 (5)	C(14)	0·004 (5)
C(12)	0·006 (5)	C(15)	−0·001 (5)
C(13)	−0·006 (5)	Nb(1)	−2·133 (4)

Plane 2: O(1), Cl(11) to Cl(13)

$$4 \cdot 553x - 7 \cdot 745y - 3 \cdot 498z = -2 \cdot 028$$

O(1)	−0·003 (2)	Cl(12)	0·001 (1)
Cl(11)	0·001 (1)	Cl(13)	−0·001 (1)
Nb(1)	0·509 (3)		

Table 5. (cont.)

Plane 3: O(1), Cl(21) to Cl(23)

$$-5 \cdot 831x - 7 \cdot 161y - 2 \cdot 873z = -3 \cdot 371$$

O(1)	−0·027 (2)	Cl(22)	0·009 (1)
Cl(21)	0·009 (1)	Cl(23)	−0·040 (3)
Nb(2)	−0·505 (8)		

Plane 4: ring C(21) to C(25)

$$5 \cdot 716x + 7 \cdot 278y + 2 \cdot 417z = 5 \cdot 836$$

C(21)	−0·005 (5)	C(24)	0·013 (5)
C(22)	0·014 (6)	C(25)	−0·008 (6)
C(23)	−0·015 (5)	Nb(2)	−2·126 (6)
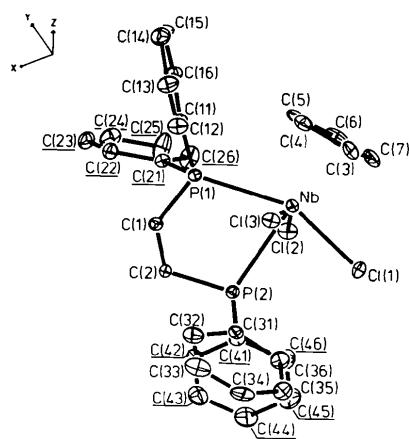
Fig. 2. The $(\eta$-C$_5$H$_5$)NbCl$_3$[(C$_6$H$_5$)$_2$(PCH$_2$)$_2$(C$_6$H$_5$)$_2$] molecule projected on to the plane defined by Nb, P(1), P(2). The ellipsoids represent 50% electron probability.

close (0·02 Å) to its centroid. The Nb—C distances range from 2·364 to 2·461 Å with no systematic variation.

Fig. 3 shows [(η-C$_5$H$_4$CH$_3$)NbCl$_3$(H$_2$O)]$_2$O, formally a complex of Nb^V, projected on to the best plane defined by O(11), O(21), Cl(11) and Cl(21). Each part of this dimer has a similar geometry to that of (I), with the water molecule replacing P(2) and the bridging O atom replacing P(1). The oxo bridge is nearly symmetrical [Nb(1)—O(1) 1·901, Nb(2)—O(1) 1·926 Å] but significantly non-linear [Nb(1)—O(1)—Nb(2) 171·8°]. The O(11)—Nb(1)···Nb(2)—O(21) torsion angle is 75·1°, very close to that in {[(η-C$_5$H$_5$)$_2$-NbCl]$_2$O}(BF$_4$)$_2$ (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The Nb atom is displaced 0·507 Å (mean value) from the plane of the three Cl atoms and O(1) towards the cyclopentadienyl ring.

The Nb—Cl bonds are 2·486, 2·450 and 2·436 Å (mean values for both parts of the dimer). Although similar values of 2·43 and 2·46 Å were observed by Kamenar & Prout (1970) in (dipy)NbO(OEt)Cl$_2$, the Nb—Cl bonds are longer than those normally found in

Table 6. *Non-bonded intramolecular contacts* <4 Å *about atoms surrounding the* Nb *atom* (Å)

(a) Compound (I)

Cl(1)···Cl(2)	3·355 (2)	Cl(1)···C(3)	3·322 (6)
Cl(1)···Cl(3)	3·426 (2)	Cl(1)···C(6)	3·880 (7)
Cl(1)···P(2)	3·372 (5)	Cl(1)···C(7)	3·059 (7)
Cl(2)···P(2)	3·198 (2)	Cl(2)···C(5)	3·622 (6)
Cl(2)···P(1)	3·715 (2)	Cl(2)···C(6)	3·069 (6)
Cl(3)···P(1)	3·341 (2)	Cl(2)···C(7)	3·622 (5)
Cl(3)···P(2)	3·213 (2)	Cl(3)···C(3)	3·122 (5)
		Cl(3)···C(4)	3·107 (6)

(b) Compound (II)

|			
Cl(11)···Cl(13)	3·328 (2)	Cl(11)···C(11)	2·961 (5)
Cl(11)···O(1)	3·125 (3)	Cl(11)···C(12)	3·787 (5)
Cl(11)···O(11)	2·913 (3)	Cl(11)···C(15)	3·325 (5)
Cl(12)···Cl(13)	3·342 (3)	Cl(12)···C(12)	3·791 (5)
Cl(12)···O(1)	3·046 (3)	Cl(12)···C(13)	2·979 (5)
Cl(12)···O(11)	2·965 (3)	Cl(12)···C(14)	3·242 (5)
Cl(13)···O(11)	2·839 (3)	Cl(13)···C(11)	3·949 (5)
		Cl(13)···C(14)	3·180 (5)
Cl(21)···Cl(23)	3·316 (3)	Cl(13)···C(15)	3·098 (5)
Cl(21)···O(1)	3·109 (3)		
Cl(21)···O(21)	2·937 (3)	Cl(21)···C(21)	2·955 (6)
Cl(22)···Cl(23)	3·360 (3)	Cl(21)···C(22)	3·828 (5)
Cl(22)···O(1)	3·071 (3)	Cl(21)···C(25)	3·187 (6)
Cl(22)···O(21)	2·982 (4)	Cl(22)···C(22)	3·719 (5)
Cl(23)···O(21)	2·836 (4)	Cl(22)···C(23)	2·932 (5)
		Cl(22)···C(24)	3·344 (6)
		Cl(23)···C(23)	3·973 (4)
		Cl(23)···C(24)	3·126 (5)
		Cl(23)···C(25)	3·155 (6)
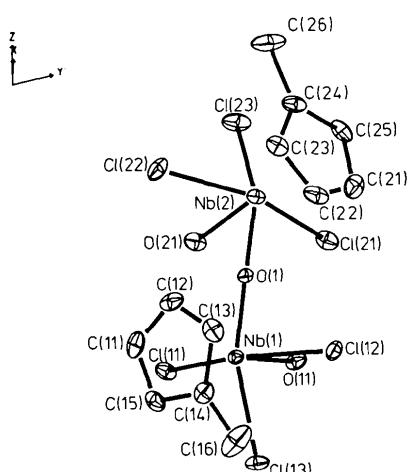
Fig. 3. The dimer complex seen projected down a direction perpendicular to the best plane of O(11), O(21), Cl(11) and Cl(21). The ellipsoids represent 50% electron probability.

Table 7. *Comparative features of* O—H ··· Cl *hydrogen-bonding systems; distances* (Å) *and angles* (°)

	O—H	O···Cl	H···Cl	O—H···Cl
(a) This study				
O(11)—H(1)···Cl(21)	0·75 (8)	3·040 (3)	2·31 (8)	162 (7)
O(21)—H(2)···Cl(11)	0·90 (7)	3·053 (3)	2·26 (7)	147 (6)
O(11)—H(3)···Cl(12)'	0·98 (7)	3·056 (3)	2·13 (7)	156 (6)
O(21)—H(4)···Cl(22)'	0·81 (7)	3·073 (3)	2·30 (7)	160 (7)
(b) [(+)Coen₃⁺(−)Cren₃⁺] Cl₆.6·1H₂O (X-ray study)				
	0·96 (16)	3·19 (1)	2·26 (20)	162 (9)
	0·89 (12)	3·26 (1)	2·39 (12)	117 (9)
(c) CuCl₂.2H₂O (neutron study)				
	0·95	3·18	2·26	164
(d) C₅H₈N₁₂.2HCl.H₂O (neutron study)				
	1·02	3·09	2·14	153
	0·99	3·15	2·19	166

(b) Whuler, Brouty, Spinat & Herpin (1976). (c) Peterson & Levy (1957). (d) Hamilton & La Placa (1968).

* en = NH₂–CH₂–CH₂–NH₂.
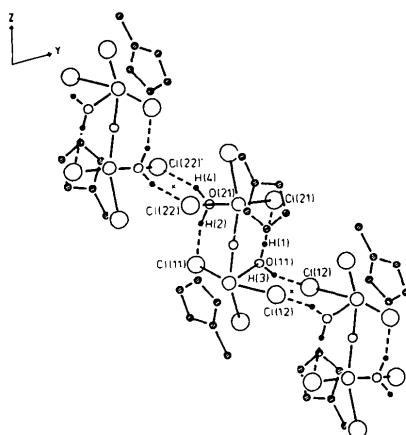
Fig. 4. Hydrogen bonding in [(η-C₅H₄CH₃)NbCl₃(H₂O)]₂O.

Nbⱽ complexes, *e.g.* 2·359, 2·338 and 2·416 Å in NbCl₃[NCH₃C(S)CH₃]₂ (Drew & Wilkins, 1974), 2·34 Å (mean value) in NbCl₃S.SPPh₃ (Drew, Fowles, Hobson & Rice, 1976), 2·35 Å (mean value) in NbOCl₃(NCCH₃)₂ (Chavant *et al.*, 1975) and 2·37 Å in {[(η-C₅H₅)₂NbCl]₂O}(BF₄)₂ (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). This lengthening

may be due to the steric repulsions between the Cl atoms and the cyclopentadienyl group; indeed, in both (I) and (II) C···Cl contacts are roughly the same (Table 6).

The remaining O atoms, O(11) and O(21), must be from water molecules because (i) all four H atoms can be found in difference maps, (ii) the H atom sites are consistent with a reasonable hydrogen-bonding pattern and (iii) any other hypothesis leads to an unreasonable valency for the central Nb atom. The water molecules are *trans* to the η-C₅H₅ rings. The Nb—O distances of 2·186 and 2·191 Å are unexceptional compared with the Nb—O single bonds to the oxalato ligands in ammonium oxotrioxalatoniobate monohydrate and ammonium diperoxodioxalatoniobate monohydrate which are between 2·11 and 2·16 Å (Mathern, Weiss

& Rohmer, 1969). The two water molecules form intra-molecular hydrogen bonds O(11)···Cl(21) and O(21)···Cl(11) and intermolecular hydrogen bonds O(11)···Cl(12)' and O(21)···Cl(22)' (Table 7) which link neighbouring dimers, making a chain along the [011] axis, Fig. 4.

In the cyclopentadienyl rings the average C–C length is 1·392 Å and the average C–C–C angle 108·0°. The Nb–C distances lie in the range 2·402 to 2·481 Å and the lengths of the normals to the rings at the Nb atoms are 2·133 and 2·126 Å respectively, surprisingly rather longer than in (I).

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The Crystal and Molecular Structure of 1,1'-Ferrocenedicarboxylic Acid (Triclinic Modification): Neutron and X-ray Diffraction Studies at 78 K and 298 K*

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Abstract

The crystal structure of the triclinic modification of 1,1'-ferrocenedicarboxylic acid, C$_{12}$H$_{10}$FeO$_4$, [Fe(η^5-C$_6$H$_5$O$_2$)$_2$], has been determined from X-ray diffraction

data measured at room temperature (298 K). Refinements based upon neutron diffraction data measured at a temperature of 78 K have provided a highly precise model. Crystal data: space group P$\bar{1}$, Z = 4, a = 7·424 (2), b = 7·809 (2), c = 18·118 (4) Å, α = 98·79 (2), β = 91·07 (2), γ = 97·21 (3)° at T = 78 K. For the neutron diffraction data, the final unweighted R value based on F^2 is 0·043 for 3856 unique reflections, and all bond distances have been determined to better