Tungsten(VI) Complexes with Citric Acid (H_4cit). Structural Characterisation of $Na_6[\{WO_2(cit)\}_2O]\cdot10H_2O$†

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The complex anion $[W_2O_5(cit)_2]^{6-}$ was obtained by crystallisation from an equimolar aqueous solution of sodium tungstate and citric acid (H_4cit). It has been characterised by elemental analysis, IR and ^1H and ^{13}C NMR spectroscopy. The IR spectrum is consistent with a monooxo-bridged dinuclear structure as revealed by a single-crystal X-ray diffraction study of $Na_6[W_2O_5(cit)_2]\cdot10H_2O$. The crystals are monoclinic, space group $P2_1/a$, $a = 17.708(3)$, $b = 9.908(2)$ and $c = 9.018(2)$ Å, $\beta = 91.57(2)^\circ$, $R = 0.025$ for 3101 observed $[I/\sigma(I) \geqslant 2.5]$ reflections. The complex anion contains a O_2WOWO_2 core with the bridging oxo group lying at a crystallographic centre of symmetry ($W-O_b-W$ 180°). Each citrate ligand is three co-ordinated to one tungsten atom through the deprotonated hydroxy, α-carboxylate, and one β-carboxylate group. Principal dimensions are: $W-O_b$ 1.893(1), $(W{=}O_t)_{av}$ 1.757(2), $W-O_{hydroxy}$ 1.958(2), $W-O_{\alpha\text{-carboxy}}$ 2.195(3) and $W-O_{\beta\text{-carboxy}}$ 2.289(2) Å. All methylene and β-carboxylate groups become magnetically equivalent upon redissolution in water as a result of the dissociation of the less strongly bonded β-carboxylate group.

As part of our systematic study of the co-ordination chemistry of molybdenum(VI) and tungsten(VI) with hydroxycarboxylic acids, complex formation in aqueous solution between sodium tungstate and citric acid (H_4cit, 3-carboxy-3-hydroxypentane-1,5-dioic acid) has been previously investigated by using polarimetric, spectrophotometric and ^1H and ^{13}C NMR techniques.[1] The pH of the medium is the principal variable controlling complex formation and interconversion equilibria. At high pH (> 6) the complexes are monomers with $(1:2:3)^{6-}$ or $(1:1:1)^{4-}$ (metal : ligand : proton) stoichiometry, while at lower pH two different dinuclear complexes with a $(2:2:4)^{6-}$ and $(2:2:7)^{3-}$ stoichiometry were observed. The results of this investigation have been partially confirmed by Cruywagen *et al.*[2] as far as the composition of the $(1:1:1)^{4-}$ and $(2:2:4)^{6-}$ complexes is concerned. We herein report the isolation and characterisation by X-ray diffraction of the $(2:2:4)^{6-}$ species which constitutes the first example of a complex with a $W_2O_5^{2+}$ core.

Results and Discussion

When sodium tungstate and citric acid are mixed to form an equimolar aqueous solution, pH 5.5, and the mixture is allowed to crystallise slowly in the presence of a small amount of Me_2SO (see Experimental section) large rhombic crystals of good quality for X-ray diffraction studies were obtained. As indicated in the Experimental section, analytical data for this complex salt are in agreement with an overall charge of −6, which is balanced by six Na^+ cations. Such a composition corresponds to a reaction stoichiometry of 2:2:4 for tungstate:citrate: hydrogen ions [equation (1)].

$$2WO_4^{2-} + 2Hcit^{3-} + 4H^+ \longrightarrow [W_2O_5(cit)_2]^{6-} + 3H_2O \quad (1)$$

Complexes containing the oxo-bridged $[M_2O_5]^{2+}$ entity are quite common in the chemistry of Mo^{VI}[3] but rather surprisingly this structure type has not been well characterised for W^{VI}.[4] Ditungsten(VI) complexes are in fact rare, and none has been previously isolated by direct reaction from tungstate and the ligand. The complexes $[W_2O_5L_2]^{2+}$ (L = 1,4,7-triazacyclononane or *N,N′,N″*-trimethyl-1,4,7-triazacyclononane) reported by Wieghardt and co-workers[5] are formed upon chemical oxidation of $[W(CO)_3L(X)]^+$ (X = F, Cl or Br) in aqueous solution. Although their structures have not yet been unambiguously characterised, they are assumed to be similar to that found in the well characterised molybdenum analogues $[Mo_2O_5L_2]^{2+}$.[6] Only the structure for $[W_2O_3(CH_2CMe_3)_6]$,[7] a tungsten(VI) complex containing an unusual OWOWO linear core, and the mixed-valence complex $[\{HB(dmpz)_3\}W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)\{HB(dmpz)_3\}]$[8] (dmpz = 3,5-dimethylpyrazolyl) have been well determined.

The Structure of $Na_6[W_2O_5(cit)_2]\cdot10H_2O$.—This complex salt crystallises in the space group $P2_1/a$ with two molecules in the unit cell. The structure and labelling scheme are presented in Fig. 1, final positional parameters in Table 1. The bridging oxygen atom O(1) is located on a crystallographic inversion centre, and half of the atomic coordinates were symmetrically generated by inversion through this centre ($W-O_b-W$ 180°). In single oxo-bridged dinuclear molybdenum(VI) complexes the Mo–O–Mo angle ranges from strictly 180° in $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ (ref. 9) to 136° in $[Mo_2O_3(O_2)_4(H_2O)_4]^{2-}$,[10] with intermediate values for $[Mo_2O_5(dmf)_4Cl_2]$ (171°) (dmf = dimethylformamide)[11] and $[Mo_2O_5(phen)_2(NCS)_2]$ (162.7°) (phen = 1,10-phenanthroline).[12]

The arrangement of atoms in the co-ordination sphere of each W atom is consistent with previous results in oxomolybdenum chemistry.[13] Therefore, each tungsten atom is co-ordinated to two unshared oxygens and these terminal and bridging oxo groups adopt *fac* stereochemistry. The remaining positions are occupied by a fully deprotonated citrate acting as a tridentate ligand with only one acetate arm co-ordinated to each metallic centre. Specifically, co-ordination occurs through O(14) of the deprotonated hydroxylate group and O(20) and O(9) of the carboxylate groups which thus form a five- and six-membered chelate ring, respectively, and complete the distorted octahedral co-ordination of W^{VI}.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

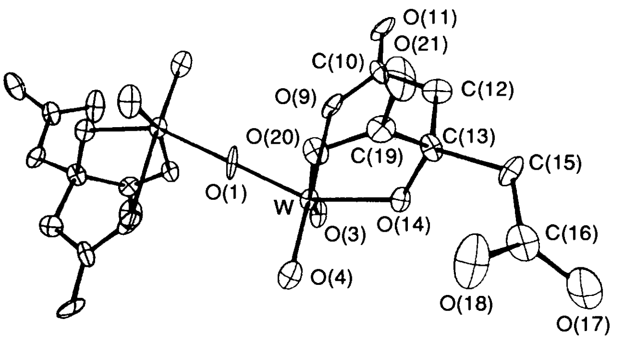

Fig. 1 An ORTEP drawing of the complex anion $[W_2O_5(cit)_2]^{6-}$ showing 50% probability ellipsoids and the atom labelling scheme

Table 1 Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations

Atom	*X/a*	*Y/b*	*Z/c*
W	5 006(2)	16 808(2)	1 948(2)
Na(1)	2 246(1)	961(2)	8 291(2)
Na(2)	2 387(1)	−152(2)	1 793(2)
Na(3)	−177(1)	929(2)	−3 520(2)
O(1)	0	0	0
O(2)	3 191(2)	−1 934(3)	2 912(3)
O(3)	450(1)	2 240(3)	−1 649(3)
O(4)	1 450(1)	1 157(3)	356(3)
O(5)	2 620(2)	−1 114(3)	−652(3)
O(6)	−1 379(2)	1 666(2)	−2 455(4)
O(7)	2 195(2)	1 010(4)	4 007(4)
O(8)	975(3)	22(6)	5 675(6)
O(9)	−742(1)	2 304(3)	294(3)
C(10)	−1 077(2)	3 301(3)	911(5)
O(11)	−1 756(1)	3 535(3)	719(4)
C(12)	−603(2)	4 261(4)	1 857(4)
C(13)	199(2)	3 817(4)	2 346(4)
O(14)	615(2)	3 494(2)	1 033(3)
C(15)	591(2)	5 002(4)	3 131(4)
C(16)	1 402(2)	4 784(4)	3 615(4)
O(17)	1 840(2)	5 812(3)	3 579(3)
O(18)	1 623(2)	3 647(3)	4 055(4)
C(19)	165(2)	2 522(4)	3 250(4)
O(20)	295(2)	1 402(3)	2 564(3)
O(21)	91(2)	−2 539(3)	5 454(3)

Compared to the μ-oxo group, the stronger *trans*-influencing ability of the multiply bonded oxygen[14] can explain the disposition of the other co-ordinated groups on the ligand wnich will arrange themselves with the weaker π-bonding donor atoms *trans* to these oxo groups. This position, *trans* to the terminal oxo groups, is considered to be occupied by the carboxylato ligand which has a sp^2 and a p type lone pair forming part of a delocalised four-electron π system. The remaining co-ordination position, *trans* to the μ-oxo group and *cis* to these terminal oxygen atoms, should be filled by the oxygen-donor atom of the alkoxy group. Therefore, the observed arrangement of the citrate ligand in this way is consistent with that previously predicted[1] on the basis of the different π-donor abilities of its donor groups.[14]

As usual for oxo complexes of Mo^{VI} and W^{VI}, the metal atom is not found at the centre of the co-ordination octahedron but is shifted toward the terminal unshared oxygen atom in a distorted-octahedral co-ordination environment. Moreover, the MO_2 group has the general property of compressing those bond angles involving other atoms to less than the octahedral values of 90 or 180°. Selected distances and angles appear in Table 2. Distances and angles within the ligand framework are unexceptional and are available as supplementary material.

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

O(1)–W	1.893(1)	O(9)–C(10)	1.287(4)
O(3)–W	1.753(2)	O(14)–C(13)	1.447(4)
O(4)–W	1.761(2)	O(20)–C(19)	1.294(4)
O(9)–W	2.289(2)	C(12)–C(10)	1.516(5)
O(14)–W	1.958(2)	C(13)–C(12)	1.538(5)
O(20)–W	2.195(3)	C(19)–C(13)	1.523(5)
$O(2)\cdots O(3^{I})$	2.811(4)	$O(6)\cdots O(17^{III})$	2.810(4)
$O(2)\cdots O(18^{II})$	2.806(4)	$O(7)\cdots O(17^{II})$	2.737(4)
$O(6)\cdots O(9)$	2.768(4)	$O(7)\cdots O(18)$	2.803(4)
W–O(1)–W	180.0	O(14)–W–O(3)	94.5(1)
O(3)–W–O(1)	100.3(1)	O(14)–W–O(4)	98.6(1)
O(4)–W–O(1)	101.1(1)	O(14)–W–O(9)	80.0(1)
O(4)–W–O(3)	101.3(1)	O(20)–W–O(1)	83.7(1)
O(9)–W–O(1)	78.0(1)	O(20)–W–O(3)	163.3(1)
O(9)–W–O(3)	85.9(1)	O(20)–W–O(4)	93.4(1)
O(9)–W–O(4)	172.9(1)	O(20)–W–O(9)	79.1(1)
O(14)–W–O(1)	152.5(1)	O(20)–W–O(14)	76.0(1)

Symmetry equivalents: I $\frac{1}{2} - x, \frac{1}{2} + y, -z$; II $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; III $-x, 1 - y, -z$.

Terminal $Mo^{VI}{=}O$ distances of ≈1.71 Å are found in $Mo_2O_5^{2+}$ complexes and in mononuclear complexes containing the MoO_2^{2+} core structure.[15] Therefore, the W=O bond lengths of 1.753(2) and 1.761(2) Å reflect considerable O→W multiple-bond character and fit well with other reported metric values for $W^{VI}{=}O$ double bonds. A pertinent example with alkoxide ligation is the monomeric complex $[W^{VI}O_2(5\text{-}Bu^tsap)(MeOH)]\cdot MeOH$[16] [$5\text{-}Bu^tH_2sap$ = 2-(5-*tert*-butylsalicylideneamino)phenol] where the W=O bond length *trans* to a co-ordinated MeOH molecule, which has a lower *trans* ability than the carboxylate, is 1.642(9) Å whereas the other W=O bond length, *trans* to a N atom with a *trans* ability comparable to that found for a carboxylate group, is 1.764(8) Å.

The bridging W–O(1) distance [1.893(1) Å] resembles the distance in $[\{HB(dmpz)_3\}W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)\{HB(dmpz)_3\}]$ (1.912 Å),[8] $[\{W^VO[S_2CN(CH_2Ph)_2]_2\}_2O]\cdot CH_2Cl_2$ (1.875 Å)[17] and in the mixed W^{VI}–W^V tetramer $Cs_5[NH_4][W_4O_8(NCS)_{12}]\cdot 6H_2O$ (average 1.867 Å).[18] However, this parameter has the longer value of 1.977 Å in $[W_2O_3(CH_2CMe_3)_6]$[7] due to the high *trans* influence exerted by the terminal W=O bonds present in the linear O=W–O–W=O core found in this complex. The W–O(1) bond length is, therefore, comparable to the distances found in other complexes containing the $Mo_2O_5^{2+}$ core, namely $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$, (1.876 Å),[9] $[Mo_2O_5(dmf)_4Cl_2]$ (1.90 Å)[11] and $[Mo_2O_5(phen)_2(NCS)_2]$ (1.1865 Å).[19]

As observed for other complexes with O-donor ligands, the single-bond $W–O_{lig}$ distances vary widely in the present complex (from 1.958 to 2.289 Å) and these variations may be ascribed to the different donor nature and *trans* and chelate effects of the co-ordinated oxygen atoms of the citrate ligand. Therefore, the relatively short $W–O_{alkoxide}$ distance [1.958(2) Å] shows that the hydroxy group is deprotonated[20] which is consistent with the distances found in *e.g.* $[W^{VI}O_2(5\text{-}Bu^tsap)(MeOH)]\cdot MeOH$[16] [1.898(8) and 1.982(9) Å]. The remaining co-ordination positions are occupied by two weak donor carboxylate groups *trans* to the oxo ligands, their bond distances to tungsten being quite different. Thus the W–O(20) distance [2.195(3) Å] is similar to the one found in $[MoO_2(Hmal)_2]^{2-}$ [H_3mal = malic acid, mean 2.243(9) Å],[21] $[MoO_2(H_2tart)_2]^{2-}$ [H_4tart = tartaric acid, 2.227(9) Å][22] and $K_4[(MoO_2)_4O_3(Hcit)_2]\cdot 6H_2O$ [2.185(5) Å][23] which, to the best of our knowledge, are the only reported oxomolybdenum(VI) complexes structurally characterised containing an α-hydroxycarboxylate ligand. The longer W–O(9) [2.289(2) Å] which implies lability to substitution is probably a result of the different donor nature of the β-carboxylate group as well as of the larger size and greater flexibility of the six-membered ring to which it belongs.

Finally, close contacts < 2.9 Å involving the water molecule

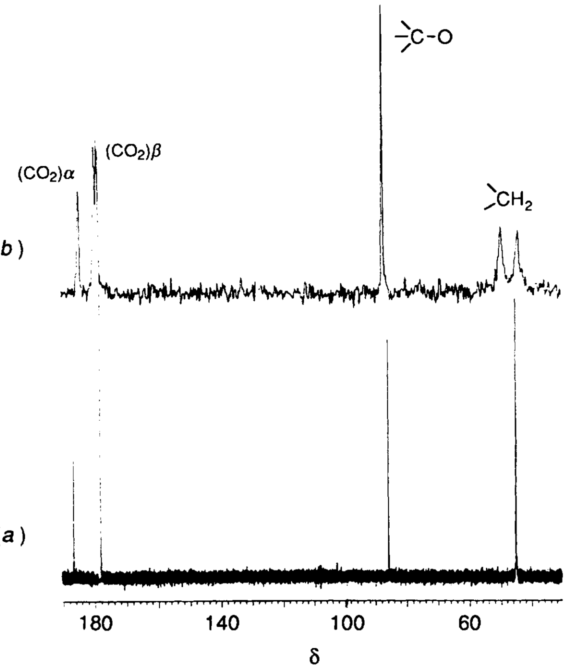

Fig. 2 (*a*) The ^{13}C NMR spectrum of $Na_6[W_2O_5(cit)_2]\cdot 10H_2O$ in D_2O; (*b*) the ^{13}C CP MAS NMR spectrum of $Na_6[W_2O_5(cit)_2]\cdot 10H_2O$

oxygen (see Table 2) and oxygen atoms from non-co-ordinated β-CO_2^- groups imply that there is some hydrogen bonding among them. Attempts to locate the hydrogen atoms in the final difference electron-density map were unsuccessful.

Spectroscopic Characterisation.—The IR spectrum of the complex $Na_6[W_2O_5(cit)_2]\cdot 10H_2O$ is similar to those of $Mo_2O_5^{2+}$ complexes which display characteristic absorptions which are useful for identifying the presence of that core. The strong band at 814 cm^{-1} is assigned to the asymmetric W–O–W stretch in agreement with previous studies.[8] There is no other band at lower energy that can be assigned to ν_{sym} stretching, consistent with a linear disposition of the bridge. The W=O bonds give rise to four bands centred around 900 cm^{-1} characteristic of the symmetric and asymmetric stretches of the *cis*-dioxo group. Finally, the presence of bands for free, 1661 cm^{-1}, and bonded, 1571 cm^{-1}, carboxylate can also be detected.

The ^{1}H NMR spectrum of the well formed crystals isolated under the conditions given in the Experimental section show only a sharp AB quartet with $\delta_A = 2.62$, $\delta_B = 2.44$ and $J_{AB} = -16.72$ Hz for methylene protons of the co-ordinated citrate ligand, whereas the large low-field shift of some ^{13}C resonances (in comparison with $Hcit^{3-}$ ions at the same pH) clearly shows that both the alcoholic (about δ 10) and α-carboxylic (about δ 5) groups are co-ordinated. The ^{1}H magnetic equivalence of the methylene groups as well as the fact that both β-carboxylate groups give only one unshifted ^{13}C NMR signal at δ 177.4 [Fig. 2(*a*)] lead us to think that the less strongly bonded β-carboxylate dissociates when the solid complex is redissolved in D_2O. Further to substantiate such an assumption, the ^{13}C cross polarisation magic angle spinning NMR spectrum in the solid state was obtained. As shown in Fig. 2(*b*), both resonances arising from acetate arms (CH_2 and β-CO_2^-) are clearly split which is consistent with the above structural findings obtained by X-ray crystallography.

Isomeric Forms.—A previous work showed that for an equimolar solution of H_4cit and Na_2WO_4 both ^{1}H and ^{13}C NMR spectra assigned to the complex $(2:2:4)^{6-}$ consist of two sets of resonances which are very similar with respect to their chemical shifts but differ very much in their intensities.[1] The spectra appear to be quite reproducible and were considered to belong to a mixture of two conformational isomers generated simply by rotation around the W–O–W bond. Integration of the ^{1}H NMR spectrum suggests a relative ratio of *ca.* 5:1 for the major and minor species. Yet, such a preliminary suggestion is not corroborated by recording the NMR spectra at different temperatures. An increase in the temperature does not show any change in the intensity of both sets of resonances.

This finding as well as the fact that in the spectra (Fig. 2) for the structurally characterised complex only the major isomer is detected with no change for more than 24 h, suggested that these species are most reasonably geometrical isomers the interconversion of which requires a bond-breaking mechanism. The formation of a pair of geometric isomers has been reported for the $[\{MoOCl[HB(pz)_3]\}_2O]$ complex system, both species being isolated and characterised. Although their structures are typical of $Mo_2O_3^{4+}$ dimers with linear Mo–O–Mo bridges they differ in the relative arrangement of the *cis*-MoOCl moiety, resulting in the overall symmetry of the complex being either C_i or C_2.[24]

For our system a new synthesis using the same pathway to that described in the Experimental section but with rapid precipitation by partial solvent elimination gave a microcrystalline solid the solution NMR spectra of which were identical to those obtained for the starting solution, with two sets of resonances. However, careful observation of this crude solid product with a magnifying lens showed large rhombic and small needle crystals. A manual separation and subsequent ^{1}H NMR characterisation indicated that the large crystals correspond to $Na_6[W_2O_5(cit)_2]$ whereas the needles ($\delta_A = 2.59$ and $\delta_B = 2.44$, $J_{AB} = -16.72$ Hz) correspond to the minor species in the solution. Although good-quality crystals of the minor isomer could not be obtained this result clearly indicates that both isomers are stable in the solid state.

Experimental

Synthesis.—A solution (10 cm^3) 0.5 mol dm^{-3} in sodium tungstate (Na_2WO_4) and 0.5 mol dm^{-3} in citric acid was adjusted to pH 5.5 with NaOH. Dimethyl sulfoxide (2–3 cm^3) was added and the mixture was left undisturbed for about 1 week at 25 °C. The compound $Na_6[W_2O_5(cit)_2]\cdot 10H_2O$ was isolated as colourless crystals. Yield: 43% (Found: C, 12.5; H, 2.5. Calc. for $C_{12}H_8Na_6O_{19}W_2\cdot 10H_2O$: C, 12.6; H, 2.4%). IR (KBr pellet): ν(W=O) 958, 918, 883, 862; ν(W–O–W) 814 cm^{-1}.

Instrumentation.—The ^{1}H and ^{13}C NMR spectra were recorded on Varian UNITY 300 and 400 spectrometers operating at 299.95 and 399.95 MHz for ^{1}H and at 75.43 and 100.58 MHz for ^{13}C. High-resolution solid-state ^{13}C NMR spectra were obtained on Varian UNITY 300, by using the combined techniques of high-power decoupling, cross polarisation (CP) and magic angle spinning (MAS) with hexamethylbenzene (δ 17.3) as external reference.

Crystal Structure Determination.—*Crystal data.* $C_{12}H_8Na_6O_{19}W_2\cdot 10H_2O$, $M = 1141.98$, monoclinic, space group $P2_1/a$ $a = 17.708(3)$, $b = 9.908(2)$, $c = 9.018(2)$ Å, $\beta = 91.57(2)°$, $U = 1581.6(9)$ Å^3, $D_c = 2.397$ g cm^{-3}, $Z = 2$, $F(000) = 1092.0$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 78.91$ cm^{-1}, $T = 298$ K.

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was mounted on a Philips PW-1100 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($8 < \theta < 12°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatised Mo-Kα radiation, using the ω–2θ scan technique. 3101 Reflections were measured in the range $2 < \theta < 25$, 2442 of which were assumed to be observed [$I > 2.5\sigma(I)$]. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed.

The structure was solved by Patterson synthesis using the SHELXS computer program[25] and refined by full-matrix least squares with the SHELX 76 program.[26] The function minimised was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0010|F_o|^2]^{-1}$. Values of f, f' and f'' were taken from ref. 27. The final R factor was 0.025 (R' = 0.026) for all observed reflections; 224 refined parameters. Maximum shift/e.s.d. = 0.1. Maximum and minimum peaks in the final difference synthesis 0.4 and −0.4 e Å^{-3}, respectively. The figure was plotted using the ORTEP program.[28]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

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