Tantalum(III)

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The reaction of tantalum tetrachloride with acetonitrile yields the diamagnetic dimer $[TaCl_3(MeCN)_2]_2$. From these acetonitrile solutions similar diamagnetic complexes $TaCl_3$(bipyridyl) and $TaCl_3$(*o*-phenanthroline), and the paramagnetic tris(dibenzoylmethanato)tantalum(III) were prepared. These are the first compounds of tantalum(III) to be characterised.

THE only known compounds of tantalum(III) appear to be the mixed valence compounds Ta_3X_8 and $(Ta_6X_{12})^{x+}$ (X = Cl, Br, or I; x = 2, 3, or 4).[1] It has been suggested,[2] on the basis of tantalum and bromine analyses only, that tantalum tetrabromide and dimethyl sulphide form ' $Ta_3Br_8,2Me_2S$ '.

Following our work [3] on the preparation of complexes of tungsten(III), we now report related work on tantalum(III).

RESULTS AND DISCUSSION

The reaction of tantalum tetrachloride with acetonitrile at 100° gives $[TaCl_3(MeCN)_2]_2$. The complex is a non-electrolyte in nitromethane and dimeric in boiling acetonitrile.

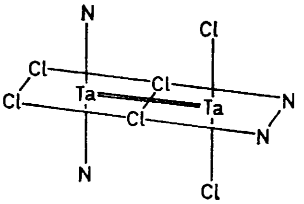
The i.r. spectrum shows five bands in the 2300 cm^{-1} region instead of the two normally observed for complexes containing co-ordinated acetonitrile (Table),[4] and indicates the presence of co-ordinated acetonitrile groups in significantly different environments. The three bands of higher energy are combination bands of the CH_3 deformation mode (ν_3) with different C–C stretching modes (ν_4), and the two at lower energy are different C–N stretching vibrations (ν_2).

I.r. spectrum of $[TaCl_3(CH_3CN)_2]_2$ (cm^{-1})

	ν_3	ν_4	$\nu_3 + \nu_4$	$\nu_3 + \nu_4$ (obs.)	ν_2
MeCN	1375	917	2292	2290	2254
$[TaCl_3(MeCN)_2]_2$	1360m	963m	2323	2321m	2284s
		950m	2310	2312s	2265s
		931m	2291	2293s	

The compound is diamagnetic and hence contains a direct tantalum–tantalum bond. Such bonding is to be expected since, as we have illustrated elsewhere, the extent of metal–metal bonding increases for metals towards the left-hand side of the periodic table, towards the bottom of the periodic table, and as the formal oxidation state is lowered.[5]

A plausible structure which fits these requirements is shown in the Figure. It is the same as that observed in the closely analogous $[WCl_3(C_5H_5N)_2]_2$.[6]



Proposed structure for $[TaCl_3(MeCN)_2]_2$

The addition of 2,2′-bipyridyl or *o*-phenanthroline to $[TaCl_3(MeCN)_2]_2$ in acetonitrile precipitates $TaCl_3$(bipy) and $TaCl_3$(*o*-phen) respectively. The i.r. spectra are normal for these complexes. Both compounds are

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[1] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247; J. H. Canterford and R. Colton, ' Halides of the Second and Third Row Transition Elements,' Wiley, London, 1968.

[2] G. W. A. Fowles, D. J. Tidmarsh, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2373.

[3] D. G. Blight and D. L. Kepert, *J. Chem. Soc.* (*A*), 1968, 534.

[4] For example, see D. L. Kepert and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2871.

[5] D. L. Kepert and R. Mandyczewsky, *Inorg. Chem.*, 1968, **7**, 2091; D. L. Kepert and K. Vrieze, ' Halogen Chemistry,' vol. 3, ed. V. Gutmann, Academic Press, London, 1967, p. 1; ' Comprehensive Inorganic Chemistry,' eds. A. F. Trotman-Dickenson, J. C. Bailar, H. J. Emeléus, and R. S. Nyholm, Pergamon Press, Oxford, in the press.

[6] R. B. Jackson and W. E. Streib, to be published. Quoted in J. L. Hayden and R. A. D. Wentworth, *J. Amer. Chem. Soc.*, 1968, **90**, 5291; R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, 1968, **7**, 1606.

again diamagnetic and non-electrolytes in nitromethane, but were insufficiently soluble to allow molecular weight determinations to be carried out. The structures presumably again involve metal–metal bonding, halogen bridges, and octahedrally co-ordinated tantalum atoms.

Dibenzoylmethane (Hdbm) and $[TaCl_3(MeCN)_2]_2$ in the presence of base precipitate $[Ta(dbm)_3]$. In contrast to the above adducts, this compound is paramagnetic with a room-temperature effective magnetic moment of 1·39 B.M. This moment is much too high for a d^1 tantalum(IV) compound,[7] but is close to the values found for octahedral d^2 tungsten(IV) compounds.[2]

We have noted elsewhere [8] that tantalum tetrachloride and dibenzoylmethane in the presence of base in acetonitrile under mild conditions form $Ta(dbm)_4$. However under other conditions tantalum(V) compounds were formed, which when either set aside or heated lose an oxygen atom from the ligand to form $[Ta^{V}Cl_3(dbm)]_2O$.[8] Although this appears to be a disproportionation reaction, we could not prepare pure tantalum(III) complexes by this technique. However the molybdenum analogue $[Mo(dbm)_3]$ could be prepared from $MoCl_4(MeCN)_2$.

Our attempts to prepare other pure tantalum(III) compounds have not yet been successful. Prolonged reaction of tantalum tetrachloride with pyridine under vigorous conditions yields only $TaCl_4(C_5H_5N)_2$, which has already been described.[9] This is in contrast to the preparation of $WCl_3(C_5H_5N)_2$ from $WCl_4(C_5H_5N)_2$.[3] No reaction was observed between $[TaCl_3(MeCN)_2]_2$ and triphenylphosphine or triphenylarsine. Oxygen abstraction was observed with dioxan to form $Ta^{V}OCl_3(diox)_2$, and also with acetylacetone and 8-hydroxyquinoline.[8] Tantalum tetrachloride and *o*-phenylenebisdimethylarsine in acetonitrile form $TaCl_4$(diars), but prolonged reaction at 200° in a sealed tube forms the eight-co-ordinate $TaCl_4(diars)_2$ and an undefined mono-adduct $TaCl_x$(diars).[7]

Other workers have studied the reactions between tantalum tetrachloride and various ligands, and have obtained either intractable tars or products which were formulated as $TaCl_4(ligand)_2$.

EXPERIMENTAL

Tantalum tetrachloride was prepared as described previously.[7] All operations were carried out under dry, oxygen-free conditions as described elsewhere.[3,7,8]

Trichlorobisacetonitriletantalum(III).—Tantalum tetrachloride (2·0 g) was refluxed with acetonitrile (40 ml) for 36 h at 100° in a sealed tube. The resulting solution was reduced in volume and the green-brown *precipitate* which formed was filtered off, washed with benzene, and dried *in vacuo* (Found: C, 12·9; H, 2·2; Cl, 28·9; Ta, 49·7. $C_4H_6Cl_3N_2Ta$ requires C, 13·0; H, 1·6; Cl, 28·8; Ta, 49·0%). The conductivity of a 10^{-3}M solution in nitromethane was 2·2 cm² ohm⁻¹. The molecular weight in boiling acetonitrile was 720 ± 20 {$[TaCl_3(MeCN)_2]_2$ requires 738}. The compound is diamagnetic, $10^6\chi_M' = -150$ c.g.s.u. The visible spectrum in dimethylformamide showed bands at 10,800 and 13,000 cm⁻¹.

Alternatively tantalum tetrachloride (3·0 g) was dissolved in acetonitrile, filtered, and the solution left for three weeks at room temperature. The small amount of green product which was deposited during this time was filtered off, washed with acetonitrile, and pumped dry (Found: Cl, 28·1%).

No reaction between tantalum pentachloride and acetonitrile occurred after several weeks in a sealed tube at 100°, suggesting that the tantalum(III) is formed by disproportionation of tantalum(IV).

Trichloro(2,2′-*bipyridyl*)*tantalum*(III).—Tantalum tetrachloride (1·0 g) was refluxed with acetonitrile (40 ml) for 36 h at 100° in a sealed tube. 2,2′-Bipyridyl (2·0 g) in acetonitrile (20 ml) was added to the solution to precipitate the pale brown *product* which was filtered off, washed with acetonitrile, and dried *in vacuo* (Found: C, 29·3; H, 2·3; Cl, 25·0. $C_{10}H_8Cl_3N_2Ta$ requires C, 27·1; H, 2·3; Cl, 24·0%). The i.r. spectrum is typical of co-ordinated bipyridyl, the out-of-plane ring deformation mode at 756 cm⁻¹ in the free ligand being split upon co-ordination with bands appearing at 770, 735, and 725 cm⁻¹.[10] The conductivity of a 10^{-3}M solution in nitromethane is 8·3 cm² ohm⁻¹ mol⁻¹. The compound is diamagnetic, $10^6\chi_M' = -160$ c.g.s.u. The diffuse-reflectance spectrum shows bands at 15,000 and 22,000 cm⁻¹.

Trichloro(o-*phenanthroline*)*tantalum*(III).—This compound was prepared in the same way as the 2,2′-bipyridyl analogue (Found: C, 30·9; H, 2·2; Cl, 22·9; Ta, 39·3. $C_{12}H_8Cl_3N_2Ta$ requires C, 31·3; H, 2·3; Cl, 23·1; Ta, 39·3%). The i.r. spectrum is typical of co-ordinated *o*-phenanthroline, with bands in the 1400—1600 cm⁻¹ region at 1447, 1465, and 1515 cm⁻¹.[11] The compound is diamagnetic, $10^6\chi_M' = -160$ c.g.s.u. The diffuse-reflectance spectrum shows bands at 15,500 and 24,000 cm⁻¹.

Tris(*dibenzoylmethanato*)*tantalum*(III).—Tantalum tetrachloride (0·4 g) in acetonitrile (100 ml) was refluxed for 3 h at 82°; triethylamine (1 ml) was added to the solution which was then filtered into a solution of dibenzoylmethane (1·0 g) in acetonitrile (50 ml). The *product* separated as small flakes on warming the solution and was filtered off, washed with acetonitrile, and pumped dry (Found: C, 62·6; H, 4·3. $C_{45}H_{33}TaO_6$ requires C, 63·6; H, 3·9%). The i.r. spectrum is very similar to that of $Ta(dbm)_4$ and other dibenzoylmethanato-complexes.[8] The room-temperature effective magnetic moment is 1·39 B.M. The diffuse-reflectance spectrum shows bands due to intraligand transitions at 43,200, 36,800, and 26,300 cm⁻¹, and to a ligand-to-metal charge-transfer transition at 14,500 cm⁻¹.[8]

Tris(*dibenzoylmethanato*)*molybdenum*(III).— Molybdenum pentachloride (0·9 g) was dissolved in acetonitrile (100 ml) and the vessel was evacuated and filled with nitrogen several times to remove hydrogen chloride produced during the formation of $MoCl_4(MeCN)_2$.[12] Triethylamine (3 ml)

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[7] R. L. Deutscher and D. L. Kepert, *Inorg. Chem.*, 1970, **9**, 2305, and references therein.

[8] R. L. Deutscher and D. L. Kepert, *Inorg. Chim. Acta*, 1970, **4**, 645.

[9] R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, 1963, **2**, 547.

[10] R. J. H. Clark, *J. Chem. Soc.*, 1963, 1377.

[11] A. A. Schiltz and R. C. Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.

[12] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531; D. L. Kepert and R. Mandyczewsky, *ibid.*, 1968, 530.

and a solution of dibenzoylmethane (3·2 g) in acetonitrile (50 ml) were added. The solution was boiled for 2 min and the black product crystallised out on cooling. The product was filtered off, washed thoroughly with acetonitrile, and pumped dry (Found: C, 68·6; H, 4·4; Cl, 0·5; Mo, 12·4. $C_{45}H_{33}MoO_6$ requires C, 70·6; H, 4·3; Mo, 12·5%). The complex had an effective magnetic moment of 3·0 B.M. [compared with 3·8 B.M. for $Mo(acac)_3$ [13]].

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[13] T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 263.