Tris(quinolin-8-olato)titanium(III). A Distorted Octahedral Monomer with an Orbitally Non-degenerate Ground State

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Tris(quinolin-8-olato)titanium(III) has been prepared by reaction of α-titanium trichloride and quinolin-8-ol in acetonitrile. Magnetic-susceptibility measurements, e.s.r. and electronic absorption spectra, and *X*-ray powder diffraction studies indicate that the complex is a distorted octahedral monomer with an orbitally non-degenerate ground state.

ALTHOUGH quinolin-8-olato-chelate compounds of most of the metals in the Periodic Table have been prepared [1,2] very few compounds with the metal in a formally low oxidation state are known.[3-8]

Structural investigations have been carried out on several metal quinolin-8-olates [$M(ox)_3$ where M = Cr, Fe, Al, Co, or Rh; (oxH) = quinolin-8-ol]. A single-crystal *X*-ray analysis of ' $Cr(ox)_3,MeOH$ ' has shown [9] that its crystal structure consists of discrete $Cr(ox)_3$

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molecules with methanol molecules trapped in cage-like cavities and that tris(quinolin-8-olato)chromium(III) has a molecular symmetry of C_1. A high-resolution n.m.r. investigation of quinolin-8-olates of aluminium, cobalt, and rhodium in dimethyl sulphoxide suggests that these compounds also exist in the *trans*-configuration in solution.[10] In contrast, Nakamoto and Ohkaku have concluded,[11] from an analysis of vibrational spectra, that tris(quinolin-8-olato)iron(III) has C_3 symmetry.

As part of an e.s.r. study of some titanium(III) complexes Smith and his co-workers [12] maintained that tris(quinolin-8-olato)titanium(III), which they did not isolate, is dimeric in solution with a metal–metal separation of 8·6 Å.

We have isolated the compound, for the first time, in our investigation of low-valent titanium complexes of quinolin-8-ol and report its preparation and some of its properties.

RESULTS AND DISCUSSION

The reaction (1) of α-titanium trichloride with excess of quinolin-8-ol in acetonitrile under vacuum resulted in the precipitation of a mixture of composition ' $TiCl_3$,6(oxH) ' which was separated into tris(quinolin-8-olato)titanium(III) and quinolin-8-olium chloride by extraction of the latter compound with de-aerated water under vacuum. *X*-Ray powder diffraction studies showed that

$$\mathrm{TiCl_3 + 6(oxH) \xrightarrow{MeCN} Ti(ox)_3 + 3(oxH)_2Cl} \qquad (1)$$

the titanium complex is isomorphous with the corresponding aluminium and chromium(III) complexes and that tris(quinolin-8-olato)iron(III) has a distinctly different powder pattern (Table 1). Thus, tris(quinolin-8-olato)titanium(III) appears to be the *mer*- rather than the *fac*-isomer.

TABLE 2

X-Ray *d*-spacings/Å for various metal tris(quinolin-8-olates)

$Ti(ox)_3$	$Cr(ox)_3$	$Al(ox)_3$	$Fe(ox)_3$
9·72vw	9·56vw	9·72vw	13·00vs
8·51vs	8·43vs	8·55vs	7·63vw
6·61w	6·53w	6·58w	6·81vw
5·70m	5·68m	5·70m	6·44m
5·52vw	5·51vw	5·52vw	5·75s
5·26vw	5·23vw	5·28vw	5·39vw
5·08vw	5·08w	5·07vw	5·13m
4·81m	4·81m	4·80m	4·60vw
4·51vw	4·51vw	4·50vw	4·27vw
4·18m	4·17m	4·18m	4·04vw
3·94s	3·94s	3·94s	3·84s
3·69m	3·69m	3·68m	3·63vw
3·60vw	3·61vw	3·57vw	3·52w
3·40vw	3·40vw	3·38vw	3·16w
3·27vw	3·27vw	3·26vw	3·08w

Tris(quinolin-8-olato)titanium(III) reacts with oxygen at room temperature to give a diamagnetic compound of composition $[Ti(ox)_3]_2O$. The half-life for the reaction (2) was *ca.* 8 min. The i.r. spectrum of $[Ti(ox)_3]_2O$

$$\mathrm{2Ti(ox)_3 + \tfrac{1}{2}O_2 \longrightarrow [Ti(ox)_3]_2O} \qquad (2)$$

contains a band at 710 cm^{-1} which is not usually observed in titanium(IV) quinolin-8-olates [13] and may be tentatively assigned to a Ti–O–Ti stretching vibration. The assignment of such vibrations is uncertain [14,15] but bands in the region of 730 cm^{-1} in the i.r. spectra of oxo-bridged dinuclear and polymeric titanium(IV) cyclopentadienyl compounds have been attributed to Ti–O–Ti stretching vibrations.[16] Our results are in line with these suggestions.

The solid and solution electronic spectra of tris(quinolin-8-olato)titanium(III) (Table 2) are very similar indicating that the same species exist in both media. The compound turns from green to purple when exposed for some time to u.v. radiation but consecutive spectra of freshly prepared samples were identical.

TABLE 2

Electronic absorption spectra of $Ti(ox)_3$ and $[Ti(ox)_3]_2O$

$Ti(ox)_3$

Diffuse reflectance $\nu_{max.}$/cm^{-1}	Solution $\nu_{max.}$/cm^{-1}	(EtOH) ε_M/l mol^{-1} cm^{-1}
31,600sh	31,600	4800
25,000s	26,000	7340
15,700s	15,300	1760
7000w,sh	7000	sh
6060w	6060	57

$[Ti(ox)_3]_2$

Diffuse reflectance $\nu_{max.}$/cm^{-1}	Solution $\nu_{max.}$/cm^{-1}	($CHCl_3$) ε_M/l mol^{-1} cm^{-1}
31,500sh	31,400	7600
24,800s	25,400	7450

The two lowest energy π→π* transitions of the quinolin-8-olato-ligand have been unambiguously assigned [17,18] and appear at *ca.* 24,600 and 31,700 cm^{-1}. The bands occurring at *ca.* 25,000 and 31,500 cm^{-1} in the spectra of $Ti(ox)_3$ and $[Ti(ox)_3]_2O$ are, therefore, attributed to these transitions. However, the possibility of a ligand-to-metal charge-transfer band in this region cannot be ruled out. Since the optical electronegativities of titanium(III) and titanium(IV) are virtually identical [19] any ligand-to-metal charge-transfer band in complexes of these ions would be expected to occur in similar positions. Accordingly, the peaks at *ca.* 15,300 and 6000 cm^{-1} in tris(quinolin-8-olato)titanium(III) which do not appear in the spectra of $[Ti(ox)_3]_2O$ can be assigned to a metal-to-ligand charge-transfer band or a *d*→*d* band with intensity stealing (15,300 cm^{-1}) and to a *d*→*d* band (6000 cm^{-1}) respectively. The position of the peak at

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6000 cm^{-1} suggests that it arises from a transition within a $^2T_{2g}$ level split by a lower-symmetry component to the ligand field rather than from a $^2T_{2g}\rightarrow{}^2E_g$ transition which would be expected at higher energy.[20]

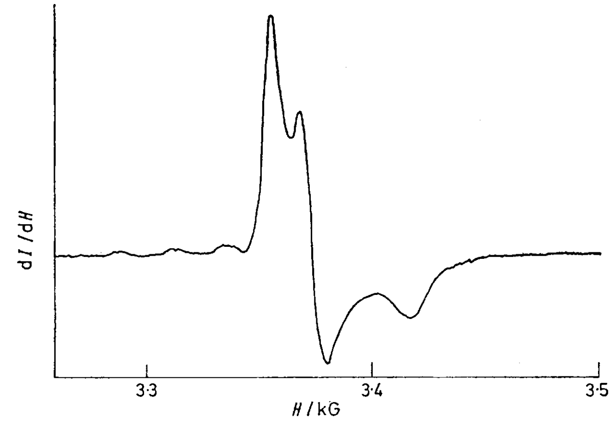

FIGURE 1 E.s.r. spectrum of Ti(ox)$_3$ in ethanol at 100 K

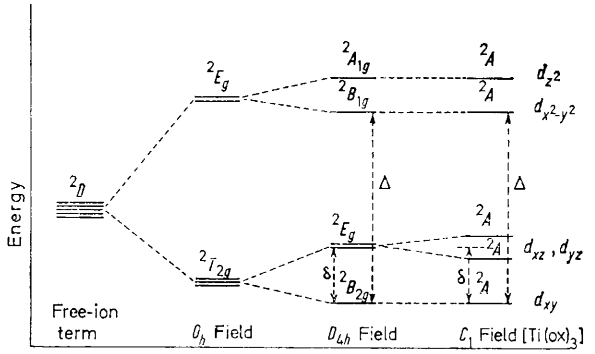

FIGURE 2 Energy-level diagram

The e.s.r. spectrum of tris(quinolin-8-olato)titanium(III) was recorded at room temperature, as a polycrystalline solid ($g_{av} = 1{\cdot}956$, linewidth = 27·3 G), as a 5×10^{-4}M solution in ethanol ($g_{av} = 1{\cdot}956$, linewidth = 9·3 G), and as 10^{-3}M solution in dimethylformamide ($g_{av} = 1{\cdot}956$, linewidth = 13·8 G). When the solutions were cooled to 100 K a three-line spectrum (Figure 1) was observed in both cases [$g_1 = 1{\cdot}974$, $g_2 = 1{\cdot}963$, and $g_3 = 1{\cdot}939$; $g_{av} = \frac{1}{3}(g_1 + g_2 + g_3) = 1{\cdot}959$] suggesting C_1 symmetry for the molecule in solution.[21] Hyperfine lines due to ^{47}Ti and ^{49}Ti were observed but could not be fully resolved into the three A_{aniso} tensor components. Assuming $g_\perp \simeq \frac{1}{2}(g_1 + g_2)$ and $g_\parallel = g_3$ we have interpreted the spectrum using Watanabe and Fujiwara's treatment[22] for a tetragonally distorted octahedral monomer. In this treatment the ground-state orbital is largely d_{xy} in character (Figure 2) and $g_\parallel$ and $g_\perp$ are calculated from equations (3) and (4) where λ = spin–orbit coupling constant of the free ion, k = orbital delocalisation constant, and δ and Δ are the energy-level separations indicated in Figure 2.

$$g_\parallel = 2{\cdot}0023 - \frac{8k\lambda}{\Delta} - \frac{3k^2\lambda^2}{(\delta + k\lambda/2)^2} - \frac{4k^2\lambda^2}{\Delta(\delta + k\lambda/2)} \quad (3)$$

$$g_\perp = 2{\cdot}0023 - \frac{2k\lambda}{(\delta + k\lambda/2)} - \frac{k^2\lambda^2}{(\delta + k\lambda/2)^2} + \frac{2k^2\lambda^2}{\Delta(\delta + k\lambda/2)} \quad (4)$$

The experimentally observed values of $g_\parallel$ and $g_\perp$ are reproduced exactly by use of equations (3) and (4) with $k = 0{\cdot}75$, $\delta = 6500$ cm^{-1}, and $\Delta = 15{,}100$ cm^{-1}; no other combination of these parameters gave satisfactory results. Attempts to obtain g values close to the experimental values by assuming a trigonal[23] rather than a tetragonal distortion were also unsuccessful.

Smith and his co-workers maintained[12] that tris(quinolin-8-olato)titanium(III) is dimeric in solution because of the presence of a ' peak ' on the high-field rather than the low-field side of the main signal. However it is possible that a tetragonally distorted monomer with a high ligand-field component along the z-axis could give rise to a ' peak ' on the high-field side if $\delta > 3000$ cm^{-1}.[22]

TABLE 3

Magnetic data for Ti(ox)$_3$

T/K	373·2	363·2	333·2	303·2
$10^6\chi_A$/c.g.s.u.	1267	1334	1428	1513
μ_{eff} [a] (B.M.)	1·72	1·75	1·75	1·73
T/K	274·2	244·5	216·7	186·1
$10^6\chi_A$/c.g.s.u.	1661	1799	1991	2286
μ_{eff} [a] (B.M.)	1·74	1·72	1·72	1·73
T/K	156·9	127·8	99·3	88·4
$10^6\chi_A$/c.g.s.u.	2632	3207	4046	4447
μ_{eff} [a] (B.M.)	1·72	1·73	1·73	1·72

$\theta = -8 \pm 2$ K.
10^6t.i.p. = 280 ± 20 (c.g.s.u.).
Diamagnetic correction = -279×10^{-6} c.g.s.u.

[a] After correction for measured temperature-independent paramagnetism (t.i.p.).

The magnetic properties of tris(quinolin-8-olato)titanium(III) are summarised in Table 3. The magnetic moment is close to the spin-only value between 370 and 90 K after correction for the experimentally determined temperature-independent paramagnetism, indicating a magnetically dilute compound with an orbitally non-degenerate ground state. The observed temperature-independent paramagnetism (Table 3) is higher than that calculated for $[\text{Ti(H}_2\text{O)}_6]^{3+}$ (84×10^{-6} c.g.s.u.)[24] and the values observed for five- and six-co-ordinate adducts of titanium trichloride and tribromide (140×10^{-6} c.g.s.u.),[25] but experimental values in the range 220×10^{-6}—350×10^{-6} c.g.s.u. have recently been reported[26] for titanium(III) cyclopentadienyl compounds.

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EXPERIMENTAL

All manipulations were carried out under vacuum or deoxygenated nitrogen by standard techniques. α-Titanium trichloride (99·9%) purity was used as obtained from Alpha Inorganics Ltd. AnalaR quinolin-8-ol was purified by sublimation (m.p. 75·5 °C; lit., 75—76 °C). All solvents were dried, distilled, and stored under vacuum.

Preparation of Ti(ox)$_3$.—α-Titanium trichloride (1·60 g, 1 mol) and quinolin-8-ol (9·03 g, 6 mol) dissolved in acetonitrile (50 ml) were stirred at room temperature under vacuum for 6 h. The green precipitate of composition 'trichlorohexakis(quinolin-8-ol)titanium(III)' (8·84 g, 0·83 mol) was filtered off, washed under vacuum with acetonitrile, and dried for 8 h at room temperature under vacuum (Found: C, 64·3; H, 4·3; Cl, 10·2; N, 8·7; Ti, 4·9. Calc. for $C_{54}H_{42}Cl_3N_6O_6Ti$: C, 63·3; H, 4·1; Cl, 10·4; N, 8·2; Ti, 4·7%). A portion of this mixture (2·17 g, 1 mol) was stirred under vacuum with water (75 ml) for 30 min. A green precipitate of tris(quinolin-8-olato)titanium(III) (0·98 g, 0·96 mol) was filtered off, washed with water under vacuum, and then dried at room temperature under vacuum for 20 h (Found: C, 67·5; H, 3·8; N, 9·2; Ti, 10·1. Calc. for $C_{27}H_{18}N_3O_3Ti$: C, 67·5; H, 3·8; N, 8·8; Ti, 10·0%). The yellow filtrate was evaporated to dryness and quinolin-8-olium chloride (1·14 g, 2·95 mol) was sublimed from the residue at 180 °C/10^{-2} mmHg (Found: C, 60·0; H, 4·4; Cl, 19·5; N, 8·4. Calc. for C_9H_8ClNO: C, 59·9; H, 4·4; Cl, 19·5; N, 7·7%).

Reaction of Ti(ox)$_3$ *with Oxygen*.—An ampoule containing tris(quinolin-8-olato)titanium(III) (0·52 g, 1 mol) was broken in an atmosphere of dry oxygen and the uptake of oxygen was monitored at room temperature with a Stanton thermobalance. The total oxygen uptake was 0·0176 g (0·25 mol) and the resulting orange solid μ-oxo-hexakis-(quinolin-8-olato)dititanium(IV) (0·54 g, 0·5 mol) was obtained [Found: C, 66·2; H, 3·6; N, 8·2; Ti, 9·9%; *M*, 948 (in chloroform). Calc. for $C_{54}H_{36}N_6O_7Ti_2$: C, 66·4; H 3·7; N, 8·6; Ti, 9·8%; *M*, 969).

Analyses were determined as described.[13,27] Molecular weights were measured at 37 °C in chloroform with a Mechrolab 301A vapour-pressure osmometer. Electronic absorption spectra were recorded on Pye–Unicam SP 700 and SP 1800 spectrophotometers; solid samples were diluted with magnesium oxide (2 : 1, v/v). E.s.r. spectra were obtained within the U.L.I.R.S. on a Decca X3 spectrometer operating in the *X*-band microwave region. Magnetic susceptibilities were determined by the Gouy method. Measurements were recorded on samples from two different preparations at 3448, 5449, 6377, and 7077 G at each temperature in the range 90—370 K. Susceptibilities did not vary with field strength and results from different preparations were in agreement within experimental error. Diamagnetic corrections were compiled from the literature [28] except for the quinolin-8-olato-anion (-90×10^{-6} c.g.s.u.) which was calculated from the experimentally determined molar susceptibility of quinolin-8-ol. *X*-Ray powder diffraction photographs were obtained from samples, sealed under vacuum in glass capillary tubes (0·01 mm diameter), in a Phillips PW 1024 Debye–Scherrer camera of 114·83 mm diameter with copper K_α *X*-radiation.

We thank Drs J. Charalambous and D. Cunningham for samples of aluminium, chromium, and iron trisquinolin-8-olates.

[2/1257 *Received*, 5*th June*, 1972]

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