Trimethyltantalum(v) Chelate Complexes †

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The interaction of dichlorotrimethyltantalum(v), Me_3TaCl_2, with sodium, potassium, or silver salts of various anions such as acetylacetonate or perchlorate that can act as bidentate or bridging ligands gave seven-co-ordinate, reasonably thermally stable, complexes of stoicheiometry $Me_3Ta(L)_2$.

The five-co-ordinate dimethylalkylamide, $Me_3Ta(NMe_2)_2$, has been prepared and shown to react with carbon disulphide which inserts only into the tantalum–nitrogen bond. The product, $Me_3Ta(S_2CNMe_2)_2$ was made independently by use of sodium dimethyldithiocarbamate. Interaction of carbon disulphide with Me_3TaCl_2 gives the eight-co-ordinate thiocarbonate $(MeCS_2)_3TaCl_2$.

Infrared and n.m.r. spectra are recorded; the species all appear to be non-rigid.

The methyl halide compounds of tantalum(v) or niobium(v), $(CH_3)_nMCl_{5-n}$, can increase their co-ordination number by formation of adducts with donor ligands or chloride ion,[1] or by insertion of neutral molecules such as NO or MeSCN.[2] However, the complete removal of chlorine has been achieved only by use of methyllithium,[3] to give $TaMe_5$, or by use of sodium or potassium salts of anionic chelates which results in a concomitant increase in the co-ordination number.[4] Details of the latter work are now given.

Although Me_3TaCl_2 and Me_5Ta are unstable at room temperature, the seven-co-ordinate complexes $Me_3Ta(L)_2$ where L is a bidentate uninegative ligand such as acetylacetonate, $acac^-$, are much more thermally stable, decomposing in the range 80—120 °C. They are, however, air sensitive causing some problems in spectroscopic and analytical measurements. It is clear that many other compounds of similar types can now be prepared. There was no substitution of chloride in Me_3TaCl_2 using KF whilst interaction of Me_3TaCl_2 with KBH_4, $NaBPh_4$, NaS_2PPh_2, and AgSCN led to decomposition; upon interaction of Me_3TaCl_2 with $Li(CH_2)_4Li$ a bright yellow solution was obtained at -78 °C which turned black above -50 °C. The complexes described here appear to be non-rigid according to variable-temperature n.m.r. studies and may also have isomers. In the absence of other structural information no attempt at detailed analysis has been made.

Oxygen Ligands.—β-*Ketoenolates.* The interaction of dichlorotrimethyltantalum(v) with two equivalents of the

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† No reprints available.

[1] G. W. A. Fowles, D. A. Rice, and T. D. Wilkins, *J.C.S. Dalton*, 1973, 961; C. Santini-Scampucci and J. G. Riess, *ibid.*, p. 2436.

[2] J. D. Wilkins and M. G. B. Drew, *J. Organometallic Chem.*, 1974, **69**, 111.

[3] R. R. Schrock and P. Meakin, *J. Amer. Chem. Soc.*, 1974, **96**, 5288.

[4] D. H. Williamson, C. Santini-Scampucci, and G. Wilkinson, *J. Organometallic Chem.*, 1974, **77**, C25.

sodium salt of a β-diketone gives the complexes $Me_3Ta(RCOCHCOR')_2$ [R = R′ = Me(acac); R = Me, R′ = CF_3(tfacac); R = R′ = CF_3(hfacac)]. The i.r. spectra of the complexes are consistent with the presence of two bidentate β-diketonate groups, *e.g.* a band at 1 555 cm^{-1} in the acac is characteristic of O-bonding.[5] The bands at 535 cm^{-1} in $Me_3Ta(acac)_2$ and 520 cm^{-1} in $Me_3Ta(tfacac)^2$ are probably the Ta–C stretches.[6] The substitution of CF_3 for CH_3 causes marked shifts of the C┈C and C┈O stretches in the ligands to higher frequencies and of the Ta–O stretching frequency to a lower frequency as found in other complexes.[7]

The ^1H n.m.r. spectra (Table 1) of $Me_3Ta(acac)_2$ and $Me_3Ta(tfacac)_2$ show sharp peaks at +35 °C, but although broadening of the Me–Ta resonance occurs on cooling to −80 °C the peaks do not split. The methyl resonances of the acetylacetonato-ligand show non-equivalence but the relative areas suggest the presence of isomers in solution. In $Me_3Ta(tfacac)_2$, the methyl on Ta as well as the methyl on C shows a broad complex pattern at 35 °C. These patterns split as the sample is cooled and at −30 °C there are three peaks for each methyl group. Detailed analyses of the spectra were not made but the observations are consistent with what would be expected for non-rigid seven-co-ordinate complexes with isomers.

TABLE 1

^1H Nuclear magnetic resonance spectra of tantalum compounds; δ in p.p.m. downfield from tetramethylsilane at 60 MHz at 35 °C, and in $CDCl_3$ or CD_2Cl_2 except where stated

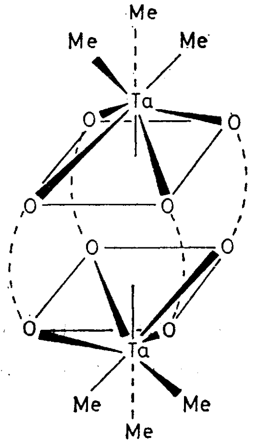
Compound	δ	Area ratio	Assignment
$Me_3Ta(acac)_2$	5.20s	2	=CH
	1.95s	12	MeC
	1.20s	9	MeTa
$Me_3Ta(tfacac)_2$	5.95s	2	=CH
	1.55br	6	MeC
	2.25s	9	MeTa
−30 °C	5.95s		=CH
	1.45	3	
	1.55m	3 } 2	MeC
	1.68	1	
	2.29	3	
	2.33m	3.5 } 3	MeTa
	2.38	2	
$Me_3Ta(hfacac)_2$	5.5s	2	=CH
	1.55s	9	MeTa
$Me_3Ta(CO_2Me)_2$	1.55s	6	MeC
	2.38s	9	MeTa
$[Me_3TaC_4O_4]_2$ [a]	1.2s		MeTa
$[Me_3Ta(ClO_4)_2]_2$ [b]	1.05s		MeTa
$Me_3Ta(pz_2BH_2)_2$	7.65d	4	
	7.15d	4	$pzBH_2$
	6.20t	4	
	1.80s	9	MeTa
$Me_3Ta(NMe_2)_2$	3.22s	12	MeN
	2.25s	9	MeTa
$Me_3Ta(S_2CNMe_2)_2$	3.325s	12	MeN
	1.37s	9	MeTa
$TaCl_2(S_2CMe)_3$	0.72s		MeC

[a] In acetone–$CHCl_3$. [b] In dioxan at 24 °C.

The mass spectrum of $Me_3Ta(acac)_2$ does not show the parent ion but peaks with successive loss of 1, 2, and 3 methyl groups are found at 409, 394, and 379, while the peak at 295 may be attributed to loss of ligand and 2 methyl groups. There are also patterns due to dissociation of $Ta(acac)_2^+$.[8] For $Me_3Ta(tfacac)_2$ the highest peak is 502 $(M - 2CH_3)^+$, while other fragments at 363 and 200 are probably TaF(tfacac) and TaF.[8]

Carboxylates. Interaction of Me_3TaCl_2 with silver acetate (or other carboxylates) gives the very light sensitive $Me_3Ta(CO_2Me)_2$ but with the trifluoroacetate extensive decomposition occurs in diethyl ether even at −78 °C.

The i.r. spectrum of the acetate in the region 1 400—1 560 cm^{-1} is consistent with bidentate carboxylate groups,[5] the multiplicity of bands arising from couplings between the groups or to the presence of isomers, while the bands at 530 and 450 cm^{-1} may be assigned respectively to the Ta–C stretch and to the Ta–O stretch of an O-bonded carboxylate.[6]



Proposed dimeric structure of trimethyltantalum squarate and perchlorate; only oxygen atoms of bridges are shown

The ^1H n.m.r. of the acetate (Table 1) shows only two singlets with the correct ratio. The Me–C resonance remains sharp at −80 °C but the Me–Ta resonance becomes very broad, indicating non-rigidity, but does not split.

Squarate. The potassium salt of squaric acid interacts with Me_3TaCl_2 to give a complex of stoicheiometry $Me_3Ta(C_4O_4)$ whose i.r. spectrum is similar to those of other squarates[9] with bands at 1 670, 1 590, and 1 505 cm^{-1}. The compound is dimeric in acetonitrile according to molecular weight determination so that it seems likely that the squarate anion is bridging (see Figure) with two oxygen atoms of each C_4O_4 unit bound to each tantalum atom. The ^1H n.m.r. at 24 °C shows only a sharp peak due to Me–Ta.

Perchlorate. The interaction of Me_3TaCl_2 and $AgClO_4$ in ether gives $Me_3Ta(ClO_4)_2$. The complex is a non-conductor (Λ = 8 Ω mol^{-1} l) and is a dimer in acetonitrile. The i.r. spectrum has strong bands at 1 185, 1 100, 1 015, and 910 cm^{-1} in accord with bidentate

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[5] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 2nd edn., 1970.

[6] See J. R. Ferraro, 'Low Frequency Vibrations of Inorganic and Coordination Compounds,' Plenum Press, New York, 1971.

[7] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, 1962, **66**, 346.

[8] M. R. Litzow and T. R. Spalding, 'Mass Spectra of Inorganic and Organometallic Compounds', Elsevier, London, 1973.

[9] R. West and H. Y. Niu, *J. Amer. Chem. Soc.*, 1963, **85**, 2589.

bridging perchlorate groups that are established in other cases.[10] The ^{1}H n.m.r. spectrum shows only a singlet that broadens at −80 °C but does not split. The compound probably has the structure in Figure 1 with four $-OCl(O_2)O-$ bridges.

Nitrogen Ligands.—Pyrazolylborate (with D. H. Williamson). Interaction of Me_3TaCl_2 in ether with two equivalents of potassium bis(pyrazolylborate) $K[pzBH_2]$ gives the yellow crystalline $Me_3Ta(pzBH_2)_2$. The i.r. spectrum shows typical bands for the pyrazolylborate [11] and additional bands assignable to Ta–C and Ta–N stretches at 504 and 481 cm^{-1}. The ^{1}H n.m.r. spectra down to −90 °C are as expected for a non-rigid structure, the $Ta-CH_3$ peak merely broadening. The pyrazolyl resonances also broaden and one, δ 7.15, is resolved into two peaks (coalescence temperature −75 °C) showing non-equivalence of the co-ordinated groups in the seven-co-ordinate complex.

Schiff bases. Using the sodium salt of bis(salicylaldehyde) ethylenedi-imine (Na_2salen) a monomeric complex Me_3Ta(salen) is obtained. The i.r. spectrum when compared with spectra of Na_2salen and literature values [12] suggest N-co-ordination of the metal by the quadridentate ligand, *e.g.* the C–N stretch is at 1 575 cm^{-1} compared to 1 630 cm^{-1} in the ligand.

Dialkylamides. The dimethylamido-complex $Me_3Ta(NMe_2)_2$, which is only five-co-ordinate, was obtained by treating Me_3TaCl_2 with $LiNMe_2$. Comparison of i.r. spectra with those of $MeTi(NMe_2)_3$ [13] and other dialkylamides [14] allows assignment of bands at 1 375 and 955 cm^{-1} as *N*-methyl vibration and bands at 1 125 and 830 cm^{-1} to methyl bound to tantalum. Bands at 560 and 530 cm^{-1} are probably TaC(N) stretches.

The ^{1}H n.m.r. spectrum has two singlets at 35 °C, that due to methyl on nitrogen showing complex splitting (7 or 8 lines between 3.32 and 2.90 p.p.m., coalescence temperature −22 °C) on cooling.

Sulphur Ligands.—Dithiocarbamate ligands. The interaction of anhydrous sodium *NN*-dialkyldithiocarbamates with Me_3TaCl_2 gives complexes $Me_3Ta(S_2CNR_2)_2$, R = Me or Pr^i. The use of thallium dithiocarbamates gave a complex reaction evidently involving an oxidation–reduction reaction and methyl transfer to thallium; one product was identified as Tl^{III} dithiocarbamate by mass spectrum.

As with the β-diketonate and carboxylate ligands both the dithiocarbamate groups are again evidently bidentate in a seven-co-ordinate complex. Thus the i.r. spectrum of $Me_3Ta(dtc)_2$ shows only one C–N band (1 510 cm^{-1} for R = Me, 1 480 cm^{-1} for R = Pr^i) and one C–S band (1 080, 1 040 cm^{-1}) as expected.[15,16] The ^{1}H n.m.r. spectrum of $Me_3Ta(S_2CNMe_2)_2$ is also consistent [15,16] with a non-rigid seven-co-ordinate species. There are sharp peaks at 35 °C and the Me–Ta resonance broadens considerably as the sample is cooled but the other peak for methyl on nitrogen stays sharp to *ca.* −60 °C indicating time averaging of this methyl resonance.[15] The isopropyl complex has a complex temperature-dependent spectrum with overlap of isopropyl- and tantalum-methyl resonances. Comparison with other spectra [15] suggests that bands at 1.53 and 1.18 p.p.m. at −30 °C are due to the methyl of the isopropyl group.

Thiocarbonate. When Me_3TaCl_2 is dissolved in carbon disulphide an orange solution is formed from which an orange-brown crystalline compound can be isolated essentially quantitatively. This is quite stable and clearly different from other compounds. It is the thiocarbonate $(MeCS_2)_3TaCl_2$ formed by CS_2 insertion into the Ta–C bond. As in other cases, *e.g.* NO insertion into hexamethyltungsten,[17] the insertion must occur successively until the maximum co-ordination number of the metal is achieved—in the present case evidently 8. That this is so is shown by the i.r. spectrum and comparison with other thiocarbonates [18] and CS_2 insertion products.[19] Thus there are only bidentate groups present since there are bands at 1 260 and 680 cm^{-1} due to C(S)S but no C–S stretches between 1 530—1 500 cm^{-1} that are expected for unidentate thiocarbonato-groups. The ^{1}H n.m.r. also has but a single line at 35 °C which as the sample is cooled broadens and splits into lines at 0.77, 0.725, 0.695, and 0.680 p.p.m. (areas 6 : 2 : 3 : 1, coalescence temperature *ca.* +1 °C). This suggests non-rigidity and the presence of isomers in solution.

Interaction of trimethylbis(dimethylamido)tantalum with carbon disulphide. In view of the insertion of CS_2 into Me_3TaCl_2 a direct comparison of the reactivities towards CS_2 insertion of Ta–C and Ta–N is possible using $Me_3Ta(NMe_2)_2$. The reaction was carried out *in situ* in an n.m.r. tube. At −20 °C the two peaks due to N–Me (3.22 p.p.m.) and Ta–Me (2.25 p.p.m.) were observed to change on injection of one equivalent of carbon disulphide and the resulting spectrum has three peaks. That due to the methyl on tantalum shows a slight upfield shift (+0.13 p.p.m.) but there is in addition to a new peak for methyl on nitrogen in NMe_2 at 2.94 a further new peak at 3.54 that can be assigned to the resonance of a S_2CNMe_2 group. When two equivalents of CS_2 are added, only two peaks are found at 3.52 and 1.98 p.p.m.; very similar to those in the complex $Me_3Ta(S_2CNMe_2)_2$ described above. Even when a further five equivalents of CS_2 are added and the mixture is set aside for more than a week at −20 °C no further change occurs. The

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[10] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, New York, 1972, 3rd edn., p. 644.

[11] S. Trofimenko, *Accounts Chem. Res.*, 1971, **4**, 17 and quoted references.

[12] K. Ueno and A. E. Martell, *J. Phys. Chem.*, 1955, **59**, 998; 1956, **60**, 1270; L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1966.

[13] H. Bürger and H. J. Neese, *J. Organometallic Chem.*, 1969, **20**, 129.

[14] M. H. Chisholm and M. Extine, *J. Amer. Chem. Soc.*, 1974, **96**, 6215; D. C. Bradley and H. M. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 980.

[15] A. N. Bhat, R. C. Ray, D. F. Lewis, A. F. Lindmark, and S. H. Strauss, *Inorg. Chem.*, 1964, **13**, 886.

[16] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 1152.

[17] A. J. Shortland and G. Wilkinson, *J.C.S. Dalton*, 1973, 872.

[18] I. S. Butler and M. E. Fenster, *J. Organometallic Chem.*, 1974, **66**, 161.

[19] L. Lindner and R. Grimm, *J. Organometallic Chem.*, 1970, **25**, 493.

n.m.r. of the isolated complex was similar to that of $\mathrm{Me_3Ta(S_2CNMe_2)_2}$ prepared from sodium dimethyldithiocarbamate. Thus under these conditions the rate of insertion of $\mathrm{CS_2}$ into the $\mathrm{Ta{-}NMe_2}$ bond must be very much faster than that into the $\mathrm{Ta{-}CH_3}$ bond. This phenomenon has been found also for insertion into $\mathrm{Me_3SnNR_2}$.[20]

EXPERIMENTAL

Microanalyses by Imperial College and A. Bernhardt. I.r. spectra in Nujol or hexachlorobutadiene were obtained using a Perkin-Elmer 577 spectrometer, n.m.r. spectra on Perkin-Elmer and Jeol instruments at 60 MHz (chemical shifts in p.p.m. downfield from $\mathrm{Me_4Si}$), and mass spectra on an AEI MS-9 spectrometer. Molecular weights were obtained using a Knauer vapour-pressure osmometer.

TABLE 2

Analytical data (%) for tantalum compounds; molecular weights in acetonitrile

	Found					Required				
Compound	C	H	N	Ta	*M*	C	H	N	Ta	*M*
$\mathrm{Me_3Ta(acac)_2}$	36.7	5.4				36.8	5.4			
$\mathrm{[Me_3Ta(C_4O_4)]_2}$	24.3	3.1		53.1	700	24.8	3.1		53.5	676
$\mathrm{[Me_3Ta(ClO_4)_2]_2}$	8.5	2.1		42.5	730	8.5	2.1		42.6	848
$\mathrm{Me_3Ta(pzBH_2)_2}$	35.1	4.8	21.5			34.7	4.6	19.2		
$\mathrm{Me_3Ta(salen)}$	45.9	4.5	5.4		500	46.3	4.7	5.7		492
$\mathrm{Me_3Ta(NMe_2)_2}$	26.1	6.4	8.8	57.5	360	26.7	6.7	8.9	57.6	314
$\mathrm{Me_3Ta(S_2CNPr^i{}_2)_2}$	34.5	6.2	4.8	22.7 (S)		35.3	6.4	4.8	22.1 (S)	
$\mathrm{TaCl_2(S_2CMe)_3}$	13.1	1.7	13.0 (Cl)	34.0		13.7	1.7	13.5 (Cl)	34.5	

All reactions were carried out under a nitrogen atmosphere or in vacuum; all solvents were dried and degassed before use. Dichlorotrimethyltantalum was made by interaction of $\mathrm{TaCl_5}$ and $\mathrm{ZnMe_2}$.[21] Anhydrous sodium salts of β-diketones and *NN′*-ethylenebis(salicylaldimine) were made by reaction of equimolar quantities of the compounds and NaH in diethyl ether. The potassium salt of 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid) was obtained by neutralisation with KOH and dehydration. Anhydrous sodium dithiocarbamates were obtained by drying over $\mathrm{P_2O_5}$ at room temperature, then at 110 °C for 3 days.[22] Silver acetate and perchlorate were dried over $\mathrm{P_2O_5}$ *in vacuo*. Lithium dimethylamide was obtained by interaction of the secondary amine and butyl-lithium.[23] Potassium dihydrobis(pyrazol-1-yl)borate was obtained by the standard method.[24] Light petroleum has b.p. 30—40 °C unless otherwise stated.

Oxygen Ligands

Trimethylbis(β-*diketonato*)*tantalum*(V).—(a) To a stirred suspension of sodium acetylacetonate (1.24 g, 10 mmol) in light petroleum (20 cm³) at −30 °C was added $\mathrm{Me_3TaCl_2}$ (0.5 g, 1.68 mmol) in light petroleum (40 cm³). After the mixture had been warmed to 25 °C and stirred for 2 h the sodium chloride was filtered off; the yellow solution was then cooled to −45 °C for 12 h. The yellow *acetylacetonato-complex* was collected, washed with light petroleum, and dried *in vacuo* (0.5 g, 70%), m.p. 83 °C (decomp); i.r.: 2 970m, 2 960m, 2 860m (νMe); 1 555s (νC$\overset{\cdot\cdot}{-}$O); 1 525s (νC$\overset{\cdot\cdot}{-}$C); 1 422s (νC$\overset{\cdot\cdot}{-}$O); 1 350s (δMe); 1 280m (νC$\overset{\cdot\cdot}{-}$C); 1 160m, 1 120sbr (δCH); 1 015sbr (ρMeCO); 945 (C-Me); 860, 840, 800br,sh (ρTaMe); 720 (ring def); 655m (δCMe), 535s (νTaC); and 440 cm⁻¹ (νTaO).

(b) Similarly prepared was the yellow-orange *trifluoroacetylacetonate*, $\mathrm{Me_3Ta(CF_3COCHCOCH_3)_2}$ (80%), m.p. 107 °C (decomp), i.r.: 2 980mbr, 2 965m, 2 815m (νMe), 1 635s (CO), 1 620s (νC$\overset{\cdot\cdot}{-}$C); 1 440br (CO); 1 410br (δCH); 1 385m, 1 365m (δMe); 1 170—1 125s,br (νC−F); 1 070—990m (ρMeCO, $\mathrm{CF_3CO}$); 860, 840, 800m (ρTaMe); 720—715sh (ring def); 590, 580 (δCMe, νTaC), and 420m cm⁻¹ (νTaO).

(c) Similarly prepared was the *hexafluoroacetylacetonate*, $\mathrm{Me_3Ta(CF_3COCHCOCF_3)_2}$ (65%), m.p. 109—110 °C (decomp); i.r.: 1 640s, (νC$\overset{\cdot\cdot}{-}$O); 480s (νTaC); and 415m cm⁻¹ (νTaO).

Bis(*acetato*)*trimethyltantalum*(V).—Light petroleum (25 cm³) was added at −78 °C to a mixture of silver acetate (0.46 g, 2.8 mmol) and $\mathrm{Me_3TaCl_2}$ (0.41 g, 1.37 mmol). After the mixture had been warmed to 25 °C and stirred for 30 min, the black residue was filtered off and the pale yellow solution cooled to −78 °C to give yellow crystals of the very light sensitive *compound* (0.31 g, 66%), m.p. 95 °C (decomp); i.r.: 2 960m, 2 920m, 2 850m (νMe); 1 560s, 1 520s ($\nu\mathrm{CO_2}$); 1 455s, 1 400s ($\nu\mathrm{CO_2}$ + δMe); 1 365m, 1 340m (δMe); 1 290m, 1 240m, 1 165m, 1 040—1 020sh,s (ρMe); 850m (ρTaMe); 720, 640s, 590s ($\delta\mathrm{CO_2}$); and 530 (νTaC), 450m, 420m cm⁻¹ (νTaO, $\rho\mathrm{CO_2}$, δCH).

μ_2-*Squarato-bis*[*trimethyltantalum*(V)].—This was prepared as were the β-diketonate compounds but using 1 : 1 ether–dichloromethane as solvent; yield 66%, and decomp. without melting 110 °C; i.r.: 1 670s, 1 590s (νCO); 1 255m, 1 180, 1 125, 1 090m,br (δCH + νCC); 1 020m, 1 015m (νCH + out-of-plane def C=CH); 855w, 790s (ρMe), 715m, 640w, 495m (νTaC); and 460 (νTaO).

μ_2-*Perchlorato-bis*[*trimethyltantalum*(V)].—This compound was prepared as the acetate from $\mathrm{Me_3TaCl_2}$ (0.5 g, 1.68 mmol) and silver perchlorate (0.83 g, *ca*. 4 mmol) but using diethyl ether to give yellow crystals of the *complex* (0.56 g, 78%), decomp. *ca*. 94 °C; i.r.: 2 980m, 2 930m (νCH); 1 455—1 445sh,m, 1 385sh,s (Me def); 1 370m, 1 330w, 1 295w, 1 260w; 1 185s ($\nu\mathrm{ClO_2}$); 1 175s (Me def); 1 145s, 1 110s ($\nu_{\mathrm{asym}}\mathrm{ClO_2}$); 1 095s, 1 015s ($\nu_{\mathrm{sym}}\mathrm{ClO_3}$); 995m, 910s ($\nu_{\mathrm{sym}}\mathrm{ClO_2}$); 880m, 830s, 820—800sh,s (ρMe); 750, 500s (νTaC); and 465m cm⁻¹ ($\mathrm{ClO_4}$ rock + sym. bend).

Nitrogen Ligands

Trimethylbis(*pyrazolylborato*)*tantalum*(V).—To $\mathrm{Me_3TaCl_2}$ (1 g, 3.36 mmol) in diethyl ether (20 cm³) at −78 °C was added potassium pyrazolylborate (1.25 g, 2 mol. equiv.) and the mixture was allowed to warm with stirring. After 2 h the yellow solution was filtered and cooled to −20 °C to give

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[20] T. A. Georges, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 1965, 2157.

[21] G. L. Juvinall, *J. Amer. Chem. Soc.*, 1964, **86**, 4202.

[22] H. L. Klopping and J. M. van der Kerk, *Rec. Trav. chim.*, 1951, **70**, 917.

[23] Houben Weyl, vol. 13, 'Metallorganische Verbindungen,' G. Thieme, Verlag, 1970, Stuttgart.

[24] S. Trofimenko, *Inorg. Synth.*, 1970, **12**, 100.

yellow crystals of the *complex* which were recrystallised from ether at −20 °C; yield 70%, decomp. 120 °C. The solutions are very air sensitive but the solid can be handled for brief periods in air.

Trimethyl[NN′-*ethylenebis*(*salicylideneiminato*)]*tantalum*(v).—To a mixture of sodium *NN′*-ethylenebis(salicylideneiminate) (0.7 g, 2.24 mmol) and Me$_3$TaCl$_2$ (0.7 g, 2.35 mmol) at −30 °C was added diethyl ether (40 cm^3) and the solution was allowed to warm with stirring. After 2 h the ether was removed and the residue extracted with dichloromethane (70 cm^3). The yellow solution was filtered and solvent removed to leave the *complex* (0.1 g, *ca.* 10%), decomp. 110 °C. I.r.: 2 960br, 2 930br, ν(CH$_3$), 2 880m, 2 870m, 2 850m ν(CH$_2$), 1 655s, 1 605s ν(C$\cdot\cdot$N), 1 580w (CC in plane), 1 550w, 1 470m (CH$_2$), 1 460s, 1 400mbr, 1 380w (νC$\overset{\cdot\cdot}{-}$N), 1 280s, 1 260s (νTaOC)?, 1 220m, 1 155—1 150sh (νTaOC), 1 100m, 1 040m, 1 020m, 980w, 855m, 800m, 755s, 750s (C–H out-of-plane def.), 740s, 720m, 610w, 530m, 500m, 490m cm^{-1} (νTa-O) + (νTa-N) + (νTa-C).

Trimethylbis(*dimethylamido*)*tantalum*(v).—To a suspension of LiNMe$_2$ (0.35 g, *ca.* 7 mmol) in diethyl ether (15 cm^3) at −35 °C was added Me$_3$TaCl$_2$ (0.91 g, 3.05 mmol) in ether (35 cm^3). The mixture was slowly warmed to −25 °C and stirred for 10 h. The white precipitate was collected by centrifugation and the yellow-orange solution evaporated at −45 °C. The yellow *complex* was washed with pentane (2 × 10 cm^3); yield 0.68 g (72%), m.p. 65 °C (decomp.). I.r. 2 960s, 2 925s, 2 900s, 2 865s—2 860sh, 2 910m, 2 860m (νTaMe+νNMe), 1 160m, 1 460s,br, 1 440m, 1 375m (νCN); 1 300w, 1 260w, 1 235w, 1 145m, 1 125m (δMe); 1 075s, 1 055s (νNC$_2$); 1 200m, 970 (νNC$_2$); 955m, 940m, 830m,br (ρTaMe); 735sh,m, 560s + 530s (νTaC + νTaN); 470w, 480w, 430w, 350w cm^{-1}.

Sulphur Ligands

Trimethylbis(*dimethyldithiocarbamato*)*tantalum*(v).— To Me$_3$TaCl$_2$ (0.8 g, 2.7 mmol) and NaS$_2$CNMe$_2$ (0.85 g, 5.9 mmol) at −78 °C was added diethyl ether (100 cm^3) and the reaction mixture was allowed to warm with stirring to 25 °C. After removal of NaCl the filtrate was evaporated and the orange *complex* washed with light petroleum (2 × 10 cm^3); yield 0.8 g (63%). I.r., 2 970m, 2 920m, 2 880m (νCH); 1 510s (νCN); 1 390 (νCN); 1 250m (νCH); 1 130, 1 080m (νCH); 980w (νCS); 790s (ρTaMe); 500m (νTaC); 420w, 395 m cm^{-1} (νTaS).

Similarly *bis*(*di-isopropyldithiocarbamato*)*trimethyltantalum*(v) was prepared from Me$_3$TaCl$_2$ (0.6 g, 2.02 mmol) and NaS$_2$CN(Pr^i)$_2$ (0.79 g, 4 mmol) to give an orange product 0.9 g (77%); i.r.: 3 005m, 2 980m, 2 940m, 2 880m, 2 810m (νMe, νCH); 1 480 (νCN); 1 358s (νCN), 1 370, 1 325s (νCMe$_2$ def); 1 195, 1 145, 1 100m (νCC + νCH); 1 040m (νCS); 805, 795s,br (ρTaMe); 500 (νTaC); 475m, 470w, 460w (ring def); 385m cm^{-1} (νTaS).

Dichlorotris(*dithiocarbonato*)*tantalum*(v).—Me$_3$TaCl$_2$ (0.3 g, 1 mmol) was added to freshly distilled CS$_2$ (10 cm^3) at −35 °C and the orange solution was stirred at 25 °C for 2 h. The solvent was removed and the *complex* was washed with pentane and dried *in vacuo*; yield 0.42 g (76%), m.p. 105—109 °C; i.r.: 2 960m, 2 930m, 2 860m; 1 455m (νCH$_3$), 1 400m (δCH$_3$); 1 260m (ν$_{\text{asym}}$CS$_2$); 1 180, 1 120m,br, 1 020m (δCH); 805w, 730—720sh,m; 680m (ν$_{\text{sym}}$CS$_2$); 430w, 380m (νTaCl); 310m cm^{-1} (νTaS).

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