Monodentate and Bidentate Behaviour of the Sulphur–Oxygen Donor Ligand Monothiothenoyltrifluoroacetone with Zerovalent Metal Carbonyls of Group VIA

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Summary Monothiothenoyltrifluoroacetone (ttas) forms two series of complexes with Group VIA zerovalent metal carbonyls in which the ligand acts as a monodentate sulphur donor or as a bidentate sulphur–oxygen donor, the two series being related by a simple carbonyl displacement

COMPLEXES of β-diketones and monothio-β-diketones are well known only for metals in normal oxidation states These compounds are usually chelates but the ligands can exhibit monodentate behaviour when forced to by bulky or stronger multidentate ligands [1]

We report here the co-ordination of ttas[2] to the zerovalent Group VI metals in which the ligand is either monodentate or bidentate depending only on the number of carbonyl groups displaced

Reaction of the thallium(I) complex of ttas with the Group VI chloropentacarbonyl-metallate(0) anions in diglyme at room temperature yields deep red, air-sensitive, diamagnetic crystalline compounds with elemental analysis correct for $NEt_4[M(CO)_5ttas]$ (I, M = Cr, Mo, W) The complexes are 1 1 electrolytes in acetone and have i r absorption bands in the terminal CO region characteristic of the octahedral $M(CO)_5L$ configuration where C_{4v} symmetry is reduced by local symmetry of the ligand[3] (Table 1) At higher temperatures the $NEt_4[M(CO)_5ttas]$ species eliminate another CO to form highly unstable, deep purple, diamagnetic $NEt_4[M(CO)_4ttas]$ (II) with CO stretching frequencies characteristic of the *cis*-$M(CO)_4L_2$ arrangement [3]

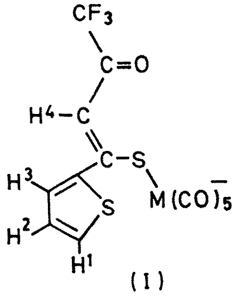
TABLE 1

Carbonyl stretching frequencies (cm^{-1})

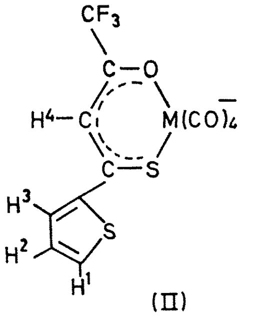
Anion	Terminal CO	β-Diketone CO
$Cr(CO)_5ttas^-$	2060(m), 1976(w), 1928(s), *ca* 1880(sh s)	1638(m)
$Mo(CO_5)ttas^-$	2064(m), 1984(w), 1937(s), *ca* 1890(sh s)	1641(m)
$W(CO)_5ttas^-$	2075(m), 1974(w) 1928(s), *ca* 1885(sh s)	1643(m)
$Cr(CO)_4ttas^-$	2008(m), 1904(s), 1870(s), 1810(s)	1612(m)
$Mo(CO)_4ttas^-$	2008(m), 1910(s), 1867(s), 1809(s)	1605(m)
$W(CO)_4ttas^-$	2016(m), 1903(s), 1855(s), 1796(s)	1600(m)

s = strong, m = medium, w = weak, sh = shoulder

The carbonyl stretching frequencies of the monothio-β-diketone show marked differences between the two series of complexes (Table 1) Compared with the free ligand, this vibration is shifted to higher frequencies in the pentacarbonyls indicating that the oxygen is not co-ordinated and that it is the sulphur atom which is linked to the metal (I)



(I)



(II)

In the tetracarbonyl complexes the shift is to lower frequencies than in the uncomplexed ligand, confirming that the oxygen is bonded to the metal and that the ligand is bidentate (II)

Monodentate sulphur co-ordination in the pentacarbonyls appears to be further supported by the proton n m r of the tungsten compound, the only one of these complexes sufficiently stable in solution to give a reliable spectrum (Table 2) This shows an upfield shift of protons 3-H and 4-H

TABLE 2

N m r absorption (*δ p p m w r t* Me_4Si)

Proton	ttas	$W(CO)_5ttas$	Shift relative to ttas
1-H	7 95	7 79	−0 16
2-H	7 23	6 95	−0 28
3-H	7 85	7 43	−0 42
4-H	7 03	6 79	−0 24

consistent with the increased localization of π-electron density in the double bonds of the ligand skeleton (I)

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