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Complexes of Thenoyltrifluoroacetone and Its Monothio Derivative with the Zerovalent Metal Carbonyls of Group VIA

G.H. Barnett and M.K. Cooper*

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The preparation and characterisation of complexes formed by the β-diketone thenoyltrifluoroacetone (tta) and its monothio analogue (ttaS) with the zerovalent Group VIA metal carbonyls is reported. The β-diketone behaves as a bidentate ligand to form $NEt_4[M(CO)_4tta]$ while the monothio ligand can act as a monodentate sulphur donor to give $NEt_4[M(CO)_5ttaS]$ or as a bidentate oxygen-sulphur donor to form $NEt_4[M(CO)_4ttaS]$. The infrared and nmr spectra of the complexes and their PPh_3 adducts are discussed with regard to current theories of bonding.

Introduction

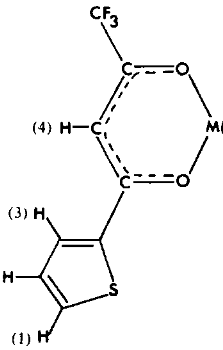
Complexes of β-diketones and monothio-β-diketones[1] have been studied for a wide range of metals in normal oxidation states but derivatives in which the metal is in an unusually low formal oxidation state are comparatively rare[2] since the metals are readily oxidised by the enolic proton of the ligand.[3] For example, the direct reaction of β-diketones with the Group VIA metal carbonyls gives only the tris-β-diketonates, M(β-dike)$_3$ (M = Cr, Mo, W), [3] in which the metal has been oxidised from the zero to the +III state.

In the course of our investigations of metal-sulphur and metal-oxygen bonding in derivatives of the Group VIA carbonyls[4] we have prepared and isolated, for the first time, β-diketone and monothio-β-diketone complexes in which the metal remains in the zero oxidation state.

The complexes of thenoyltrifluoroacetone (tta) and monothiothenoyltrifluoroacetone (ttaS) reported herein are representative of a series of substituted β-diketone metal carbonyl complexes which we are presently studying.

Results and Discussion

Reaction of the thallium(I) complex (Tltta) with a chloropentacarbonylmetallate(0) ion ($M(CO)_5Cl^-$; M = Cr, Mo, W) at room temperature gives the orange-brown, highly unstable diamagnetic complexes *cis*-$M(CO)_4tta^-$(I) which can be isolated as their tetraethylammonium salts.



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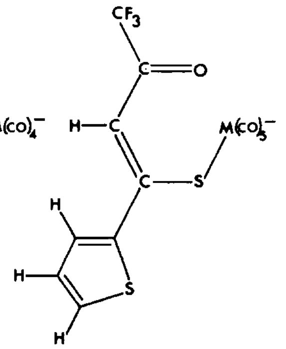
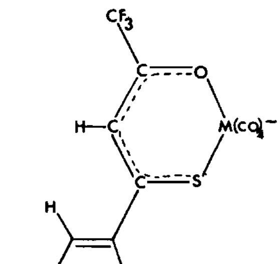


II

When the analogous reaction is performed with the monothio complex (TlttaS salts of the deep red diamagnetic anion, $M(CO)_5ttaS^-$(II), can be isolated in which the ligand is attached by the thiol sulphur donor only.[4] Solutions of these complexes evolve carbon monoxide to produce the blue (Cr) or purple (Mo, W), highly unstable, diamagnetic complexes *cis*-$M(CO)_4ttaS^-$(III) in which the ligand is bidentate. The rate of monodentate/bidentate conversion depends on the metal such that Mo > Cr > W. It is significant that this is the order of measured bond strength of the metal-carbon bonds.[5] We are at present studying the kinetics of this reaction.



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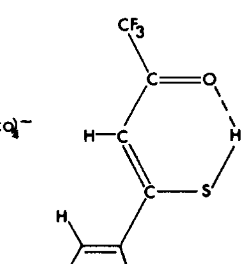

IV

(1) (a) S.H.H. Chaston, S. E. Livingstone, T.N. Lockyer, V.A. Pickles and J.S. Shannon, *Austral. J. Chem.*, *18*, 673 (1965).
(b) S.E. Livingstone, *Coord. Chem. Rev.*, *7*, 59 (1971).
(c) M. Cox and J. Darken, *ibid*, *7*, 29 (1971).
(2) (a) F. Bonati, *Organometal. Chem. Rev.* (B), *1*, 379 (1965).
(b) F. Hartmann, M. Kilner, and A. Wojcicki, *Inorg. Chem.*, *6*, 34 (1967).
(c) M. Kilner and A. Wojcicki, *ibid*, *4*, 591 (1965).
(3) (a) J.C. Goan, C.H. Huether and H.E. Podall, *ibid*, *1*, 856 (1962).
(b) M.L. Larson and F.W. Moore, *ibid.*, *1*, 856 (1962).
(c) T.G. Dunne and F.A. Cotton, *ibid.*, *2*, 1078 (1963).
(4) G.H. Barnett and M.K. Cooper, *Chem. Commun.*, 1082 (1971).
(5) D.R. Lloyd and E.W Schlag, *Inorg Chem.*, *8*, 2544 (1969).

Table I. Analytical Results.

Compound	Colour	Conductivity [a]		C	H	N	S	F	P	Metal
$NEt_4[Cr(CO)_5ttaS]$	deep red	117	Calc.	45.08	4.32	—	11.5	10.2	—	9.5
			Found	44.92	4.40	—	11.1	9.7	—	9.4
$NEt_4[Cr(CO)_4ttaS]$	deep blue	127	Calc.	45·12	4.53	2.63	12.0	—	—	—
			Found	44.80	4.68	3.07	11.7	—	—	—
$NEt_4[Cr(CO)_3(PPh_3)ttaS]$	green	120	Calc.	58.03	5.13	—	—	—	4.0	—
			Found	56.60	5.18	—	—	—	3.7	—
$NEt_4[Mo(CO)_5ttaS]$	deep red	118	Calc.	41.72	3.97	—	10.6	9.4	—	23.9
			Found	41.24	4.04	—	9.4	9.0	—	23.4
$NEt_4[Mo(CO)_4ttaS]$	purple	115	Calc.	41.74	4.20	2.43	—	—	—	26.7
			Found	41.74	4.41	2.68	—	—	—	27.1
$NEt_4[Mo(CO)_3(PPh_3)ttaS]$	blue		Calc.	50.37	4.94	1.73	7.9	7.0	—	—
			Found	50.74	5.12	1.20	7.8	6.6	—	—
$NEt_4[W(CO)_5ttaS]$	deep red	114	Calc.	36.48	3.50	2.03	9.3	—	—	26.6
			Found	36.45	3.76	2.46	8.9	—	—	27.0
$NEt_4[W(CO)_4ttaS]$	purple		Calc.	36.21	3.65	2.11	9.7	—	—	27.7
			Found	35.75	3.72	2.07	9.3	—	—	27.0
$NEt_4[W(CO)_3(PPh_3)ttaS]$	blue	124	Calc.	49.51	4.38	1.56	7.1	—	3.5	—
			Found	48.46	4.37	1.29	6.5	—	3.3	—
$NEt_4[Cr(CO)_4tta]$	brown	99	Calc.	46.60	4.69	—	6.2	—	—	10.1
			Found	46.46	4.69	—	6.3	—	—	10.7
$NEt_4[Cr(CO)_3(PPh_3)tta]$	plum	120	Calc.	59.26	5.24	1.87	4.3	4.1	—	—
			Found	60.48	5.50	2.09	3.9	3.8	—	—
$NEt_4[Mo(CO)_4tta]$	brown		Calc.	32.94	3.29	2.50	—	—	—	20.08
			Found	32.64	3·43	2.49	—	—	—	20.41
$NEt_4[Mo(CO)_3(PPh_3)tta]$	red	103	Calc.	55.99	4.95	1.76	4.0	—	3.9	—
			Found	55.96	5.52	1.88	3.9	—	3.6	—
$NEt_4[W(CO)_4tta]$	brown		Calc.	37.09	3.73	2.16	5.0	—	—	28.4
			Found	36.85	3.50	2.20	4.6	—	—	27.5
$NEt_4[W(CO)_3(PPh_3)tta]$	red	91	Calc.	50.41	4.46	1.59	3.6	6.5	3.5	—
			Found	49.42	4.89	1.39	3.6	6.2	3.3	—

[a] $ohm^{-1} . cm^2 . mole^{-1}$.

Table II. 60 MHz Nmr spectra of the tungsten complexes in THF solution (Chemical shifts in δ p.p.m. from TMS).

(a) ttaS Complexes	H-1	H-2	H-3	H-4
ttaS(H)	7.95	7.23	7.95	7.17
$W(CO)_5ttaS^-$	7.79	6.95	7.43	6.79
Shift relative to ttaS	—0.16	—0.28	—0.52	—0.38
$W(CO)_4ttaS^-$	7.70	7.04	7.62	6.95
Shift relative to ttaS	—0.25	—0.19	—0.33	—0.22
$W(CO)_3(PPh_3)ttaS^-$	7.43	6.88	7.43	6.32
Shift relative to ttaS	—0.52	—0.35	—0.52	—0.85
(b) tta Complexes				
tta(H)	7.89	7.17	7.89	6.58
$W(CO)_4tta^-$	7.70	7.07	7.63	6.22
Shift relative to tta	—0.19	—0.10	—0.26	—0.36
$W(CO)_3(PPh_3)tta^-$	7.53	6.63	7.40	5.70
Shift relative to tta	—0.36	—0.54	—0.49	—0.88

All the complexes react with triphenylphosphine to form the *cis*-tricarbonyl derivatives, $M(CO)_3(PPh_3)L_2^-$, where $L_2^- =$ tta, ttaS. The molybdenum and tungsten tricarbonyl complexes are unstable in solution and, in the absence of excess PPh_3, undergo dissociation to form the parent tetracarbonyls, whilst the chromium complexes tend to disproportionate both in solution and in the solid state to form *trans*-$Cr(CO)_4(PPh_3)_2$.[6] These products were readily identified by their CO stretching bands in the infrared.

The tta and ttaS complexes and their phosphine derivatives are soluble in highly polar organic solvents and insoluble in water, ether and light petroleum. They are 1:1 electrolytes in acetone solution (Table I).[7]

Nmr spectra. The nmr spectra of the ttaS complexes are consistent with variations in the degree of electron delocalisation as the ligand changes from monodentate to bidentate coordination. Comparison of the nmr spectra of ttaS and $W(CO)_5ttaS^-$ (Table II) shows that all the protons move upfield on complexation indicating a decrease in π electron delocalisation throughout the ligand. The order of increase of the upfield shifts of protons H-1, H-2 and H-3 suggests that the thiol sulphur is coordinated. Bonding through the oxygen might be expected to effect H-4 more than H-3.

In the tungsten tetracarbonyl complex (III), the protons all shift upfield by a similar amount relative to the free (protonated) ligand (IV). H-3 and H-4 are less affected than in the corresponding pentacarbonyl complex indicating that the ligand is more delocalised (structures (III) and (IV) are analogous).

The complex $W(CO)_4tta^-$ also exhibits an upfield shift of all the protons relative to tta but H-4 experiences a larger shift than in the analogous ttaS complex (III). This may be due to some degree of π back-donation to the sulphur from the metal, which does not occur in the metal-oxygen bond. Such π back-donation should result in a greater contribution from the structure shown in Fig. 1 (b) to the resonance hybrid.

When a carbonyl group in the complexes (I) and (III) is replaced by PPh_3, all the proton resonances

(6) F.A. Cotton and C.S. Kraihanzel, *J. Amer. Chem. Soc.*, *84*, 4432 (1962).
(7) W.J. Geary, *Coord. Chem. Rev.*, *7*, 81 (1971).

Table III. Carbonyl Stretching Frequencies (cm^{-1}) in CH_2Cl_2 solution.

Complexes	Frequencies					Force constants			
(a) *tta complexes*	A_1^1	B_1	A_1^2	B_2	β-dike	k_1	k_2 [c]	k_c	k_c'
$Cr(CO)_4tta^-$	2003	1889	1852	1795	1601	13.55	15.20	0.39	0.39 [a]
	(m)	(s)	(s)	(s)	(m.s)	13.58	15.18	0.38	0.57 [b]
$Mo(CO)_4tta^-$	2008	1894	1850	1792	1596	13.51	15.27	0.40	0.40 [a]
	(m)	(s)	(s)	(s)	(m.s)	13.53	15.25	0.38	0.54 [b]
$W(CO)_4tta^-$	2003	1882	1843	1785	1592	13.41	15.12	0.42	0.42 [a]
	(m)	(s)	(s)	(s)	(m.s)	13.42	15.11	0.40	0.56 [b]
(b) *ttaS complexes*	A_1^2	B_1	E	A_1^1	β-dikeS	k_1	k_2 [c]	k_c	
$Cr(CO)_5ttaS^-$	2060	1976	1928	1880	1638	14.49	15.77	0.38 [a]	
	(w)	(w)	(v.s)	(m.sh)	(m.w)				
$Mo(CO)_5ttaS^-$	2064	1984	1937	1890	1641	14.63	15.89	0.37 [a]	
	(w)	(w)	(v.s)	(m.sh)	(m.w)				
$W(CO)_5ttaS^-$	2060	1974	1929	1880	1643	14.49	15.76	0.38 [a]	
	(w)	(w)	(v.s)	(m.sh)	(m.w)				
	A_1^1	B_1	A_1^2	B_2	β-dikeS	k_1	k_2 [c]	k_c	k_c'
$Cr(CO)_4ttaS^-$	2008	1904	1870	1810	1612	13.77	15.36	0.37	0.37 [a]
	(m)	(s)	(s)	(s)	(m.w)	13.80	15.34	0.35	0.57 [b]
$Mo(CO)_4ttaS^-$	2008	1909	1866	1808	1605	13.72	15.41	0.35	0.35 [a]
	(m)	(s)	(s)	(s)	(m.w)	13.74	15.39	0.33	0.54 [b]
$W(CO)_4ttaS^-$	2005	1899	1860	1800	1600	13.62	15.29	0.38	0.38 [a]
	(m)	(s)	(s)	(s)	(m.w)	13.64	15.28	0.36	0.55 [b]

[a] Calculated by the method of Cotton and Kraihanzel.[6] [b] Calculated by the method of Delbeke *et al.*[9] [c] k_1 refers to CO groups *trans* to the ligand, k_2 to CO groups *cis* to the ligand (m.dyne/Å). (s) = strong (m) = medium (w) = weak (sh.) = shoulder.

move further upfield with H-4 experiencing the greatest upfield shift. Since PPh_3 is a stronger σ donor than CO and (in d^6 complexes) a weaker π acid,[8] this upfield shift can be explained in terms of forcing electron density back onto the O and S donor atoms

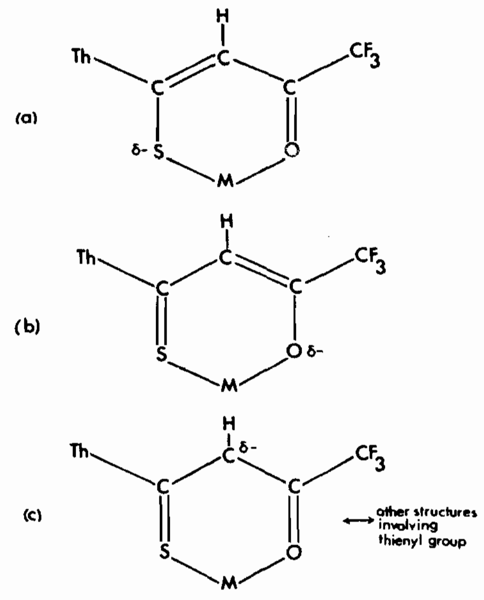

Figure 1. Resonance forms of ttaS in metal complexes.

of the ligands when CO is replaced by PPh_3, resulting in the build up of negative charge on the carbon atom attached to H-4 and hence shielding H-4 (Figure 1c).

Infrared spectra. (a) *The Region* 2100-1500 cm^{-1} The carbonyl stretching frequencies of the complexes (I) and (III) are shown in Table III. These are characteristic of octahedral *cis*-$M(CO)_4L_2$ compounds with C_{2v} symmetry.[5] We have assigned the modes on the basis of force constants by using the procedures outlined by Cotton and Kraihanzel[6] and Delbeke et al.[9] The two methods give comparable values of the stretching force constants k_1 and k_2 for the *trans* and *cis* carbonyls respectively (Table III).

Another strong peak appears in the spectra of these complexes at ca. 1600 cm^{-1} which we have assigned to the ketonic carbonyl group of the β-diketone or monothio-β-diketone.[1]

The terminal carbonyl stretching frequencies of the pentacarbonyls (II) are characteristic of octahedral C_{4v} symmetry. The appearance of the formally forbidden B_1 mode as a weak shoulder near 1970 cm^{-1} is probably due to the asymmetry of the ligand ttaS,[6] although other explanations have been suggested[10] for the appearance of this mode in similar complexes.

The absorption of medium intensity at ca. 1640 cm^{-1} may be assigned to the ketonic carbonyl group of the monothio-β-diketone.[11a]

The position of the ketonic CO stretch in the infrared spectra ofthe penta- and tetracarbonyls of ttaS

(8) L.D. Pettit, *Quart. Rev.*, 25, 1 (1971).

(9) (a) F.T. Delbeke, E.G. Claeys, R.M. Caluwe and G.P. Van der Kelen, *J. Organometal. Chem.*, 23, 505 (1970). (b) F.T. Delbeke, E.G. Claeys, and G.P. Van der Kelen, *ibid.*, 25, 219 (1970).
(10) M.Y. Darensbourg and D.J. Darensbourg, *Inorg. Chem.*, 9, 32 (1970).
(11) (a) R.K.Y.Ho, S.E. Livingstone and T.N. Lockyer, *Austral. J. Chem.*, 21, 103 (1968). (b) M.A. Bush, D.E. Fenton, R.S. Nyholm, and M.R. Truter, *Chem. Commun.*, 1335 (1970).

Table IV. Solvent Dependence of Infrared Frequencies. (ν(C-O) in cm^{-1}).

Complex	Frequencies					Medium	ε [b]
	A_1^1	B_1	A_1^2	B_2	β-dikeS		
$Mo(CO)_4ttaS^-$	2012	1911	1861	1800	1600	$CHCl_3$	4.81
	2008	1909	1866	1808	1605	CH_2Cl_2	9.08
	2008	1904	1874	1816	1605	acetone	20.70
	2008	1905	1874	1815	1605	THF	—
	2020	1912	1853	1793	1598	Nujol	—
	A_1^2	B_1	E	A_1^1	β-dikeS		
$W(CO)_5ttaS^-$	2070	1977	1932	1885	1630	$CHCl_3$	4.81
	2060	1974	1929	1880	1643	CH_2Cl_2	9.08
	2057	1967	1921	1882	1640	acetone	20.70
	2080	[a]	[a]	[a]	1624	KBr disc	—

[a] Solid state effects cause extra bands. [b] Dielectric const.[17]

Table V. Carbonyl Stretching Frequencies of PPh_3 Adducts in CH_2Cl_2 solution (ν(C-O) in cm^{-1}).

Complex	A′	A′	A″
$Cr(CO)_3(PPh_3)tta^-$	1888	1803	1770
$Mo(CO)_3(PPh_3)tta^-$	1890	1792	1756
$W(CO)_3(PPh_3)tta^-$	1885	1777	1741
$Cr(CO)_3(PPh_3)ttaS^-$ [a]	1903	1820	1795
$Mo(CO)_3(PPh_3)ttaS^-$	1906	1808	1775
$W(CO)_3(PPh_3)ttaS^-$	1900	1802	1763

[a] THF solution (unstable in CH_2Cl_2).

Table VI. Symmetric and Asymmetric Vibrations of the CF_3 groups in Nujol mull. (ν(C-F) in cm^{-1}).

Compound	Sym.	Asym.
tta	1201	1160
$Cr(CO)_4tta^-$	1182	1132
$Mo(CO)_4tta^-$	1188	1144
$W(CO)_4tta^-$	1190	1145
$Cr(CO)_3(PPh_3)tta^-$	1182	1127
$Mo(CO)_3(PPh_3)tta^-$	1180	1128
$W(CO)_3(PPh_3)tta^-$	1182	1130
ttaS	1201	1143
$Cr(CO)_5ttaS^-$	1188	1134
$Mo(CO)_5ttaS^-$	1188	1125
$W(CO)_5ttaS^-$	1189	1135
$Cr(CO)_4ttaS^-$	1180	1131
$Mo(CO)_4ttaS^-$	1180	1120
$W(CO)_4ttaS^-$	1181	1132
$Cr(CO)_3(PPh_3)ttaS^-$	1170	1117
$Mo(CO)_3(PPh_3)ttaS^-$	1170	1125
$W(CO)_3(PPh_3)ttaS^-$	1171	1129

relative to the free ligand (1621 cm^{-1}) is diagnostic of the mode of coordination.[11] In the pentacarbonyls the band occurs at higher wavenumber which suggests monodentate sulphur coordination while in the tetracarbonyls it occurs at lower wavenumber indicating bidentate chelation.

Further evidence that the ketonic carbonyl group is not coordinated in the pentacarbonyl complexes is obtained from the solvent dependence of the infrared spectra of both tta and ttaS complexes (Table IV). The uncoordinated ketonic CO group is affected markedly by the solvent while the coordinated ketonic CO groups in the tta and ttaS tetracarbonyls are relatively insensitive to changes in solvent. This shows that the ketonic CO groups of the two types of complexes are in different environments an substantiates the monodentate sulphur coordination in the pentacarbonyls.

The phosphine substituted tricarbonyl complexes of tta and ttaS exhibit three terminal CO stretching bands in the 2100-1500 cm^{-1} region, corresponding to the 2A′ and A″ modes of C_s symmetry (Table V).[6] The highest A′ mode is very close in frequency to the B_1 mode of the parent tetracarbonyl although it is symmetry related to the $A_1{}^1$ mode (Figure 2).

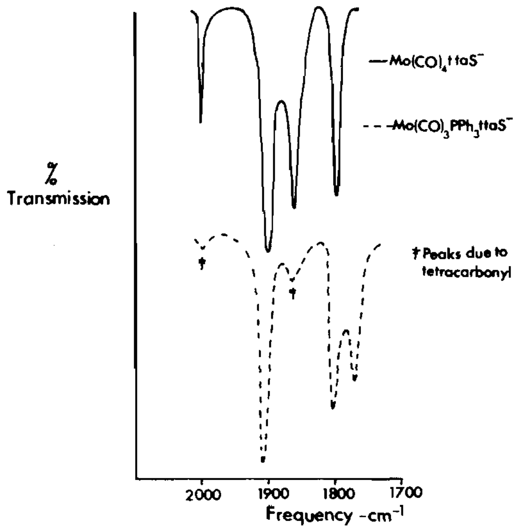

Figure 2. Comparison of the infrared spectra of tri- and tetracarbonyl derivatives of ttaS.

The shift to higher frequency results from the additional component due to the stretching of the CO group *trans* to PPh_3. The second A′ mode is equivalent by symmetry to the B_2 mode of the tetracarbonyls and is observed at almost the same frequency.

(b) *The Region* 1500-700 *cm* $^{-1}$. The only readily assigned bands in this region are those of the CF_3

Table VII. Positions and Relative Intensities of ν(M-C) and δ(M-C-O).

Complex	ν(M-C) (cm^{-1})			δ(M-C-O) (cm^{-1})			
	B_1 [a]	A_1	A_1				
$Cr(CO)_4tta^-$ [b]	389,380 (s)	430 (m)	—	688 (w)	655 (m)	619 (m.s.)	589 (w)
$Cr(CO)_4tta^-$ [c]	397,375 (s)	435 (m)	—	680 (w)	652 (m)	620 (m.s.)	585 (w)
$Mo(CO)_4tta^-$ [b]	335 (v.s)	370 (w)	399 (w)	640 (w.sh)	617 (m.w.)	570 (m.s.)	519 (w)
$W(CO)_4tta^-$ [c]	348 (s)	415 (m)	—	655 (w)	600 (m)	570 (m)	524 (w)
$Cr(CO)_4ttaS^-$ [b]	405 (m)	435 (m)	—	679 (m)	645 (m)	630 (m)	612 (m)
$Mo(CO)_4ttaS^-$ [b]	338 (s)	285 (w)	400 (w)	639 (m)	603 (m)	574 (m)	559 (m)
$W(CO_4ttaS^-$ [b]	355 (s)	400 (w)	—	621 (m)	596 (m)	578 (m)	562 (m)
	E [a]	A_1					
$W(CO)_5ttaS^-$ [b]	383 (s)	421 (w)		620 (w)	600 (s)	586 (s)	530 (w)
$W(CO)_5ttaS^-$ [c]	372 (s)	415 (w)		635 (w)	602 (s)	580 (s)	530 (w)
$Mo(CO)_5ttaS^-$ [b]	350 (s)	395 (w)		600 (s)	542 (s)	—	—
$Mo(CO)_5ttaS^-$ [c]	365 (s)	395 (w)		582 (s)	555 (m)	—	—
$Cr(CO)_5ttaS^-$ [b]	452 (m)	533 (m)		668 (s)	657 (s)	—	—

[a] May be coupled with ν(M-O)/ν(M-S). [b] Solid state (Nujol mull). [c] Solution (CH_2Cl_2) v = very, s = strong, m = medium, w = weak, sh = shoulder.

group. Table VI shows C–F symmetric and asymmetric vibrations[12] for the complexes of tta and ttaS, compared to the free ligands. Both frequencies decrease on coordination. In the ttaS complexes the decrease is greatest for the tricarbonyls and least for the pentacarbonyls. Similarly the tta tricarbonyls show a greater shift in this frequency than the corresponding tetracarbonyls.

The tetracarbonyl and tricarbonyl complexes are expected to give rise to lower CF_3 vibrational frequencies than the pentacarbonyls, since this group is closer to the site of coordination in the former compounds. The further shifts which occur when PPh_3 is substituted for CO correlate with the changes in delocalisation inferred from the nmr spectra. Increased localisation of charge (Figure 1(c)) throughout the ligand would result in accumulation of δ+ charge adjacent to the CF_3 group, causing σ withdrawal of electron density from the C–F bond.

Although the CF_3 groups are well removed from the site of coordination they are nevertheless sensitive to variations in metal-ligand bonding.

(c) *The Region* 700-250 cm^{-1}. Absorptions corresponding to ν(M–C), δ(M–C–O) and ν(M–L) occur in this range, [13] and we have made tentative assignments (Table VII) of some of these bands by comparison with other β-diketone and monothio-β-diketone carbonyl complexes.[14] To assist us in making these assignments we have attempted to apply the general rules[13] that, (a) ν(M–C) + ν(C–O) = constant, (b) δ(M–C–O) occurs at higher frequency than ν(M–C).

We also expect some coupling between the symmetry related modes of ν(M–S), ν(M–O) and ν(M–C). For example it is very likely that the intense B_1 M–C stretching mode contains a considerable contribution from ν(M–O).

The M–C stretches for the tta and ttaS tetracarbonyl complexes are difficult to correlate, in that these bands occur at higher wavenumber in the ttaS complexes than in the tta analogues whereas the rule (a) would predict the opposite effect. This unexpected order of the M–C bands has been noted in other systems. For example, in the complexes $M(CO)_5L$ where L represents a series of ligands with different donor atoms the expected reciprocal dependence of ν(C–O) (E mode) on ν(M–C) (E mode) was not observed.[15] A rationalisation of this was put forward by Brown and Dobson on the basis of Fenske and DeKock's concept[16] of "direct donation" from ligand σ orbitals into the π* orbitals of the *cis* carbonyl groups.

Solvent Dependence of Infrared Spectra. A plot of the terminal carbonyl stretching frequencies of $Mo(CO)_4ttaS^-$ (Table IV) against $\frac{\varepsilon-1}{\varepsilon+2}$ [12b] where

(12) (a) L.J. Bellamy "The Infrared Spectra of Complex Molecules" Methuen (1966).
(b) C.N.R. Rao "Chemical Applications of Infrared Spectroscopy" Academic Press, New York and London, 1963.
(13) D.M. Adams "Metal-Ligand and Related Vibrations" Arnold London, 1967.
(14) M.K. Cooper and G.H. Barnett, unpublished results.
(15) R.A. Brown and G.R. Dobson, *Inorg. Chim. Acta*, *6*, 65 (1972).
(16) (a) R.F. Fenske and R.J. DeKock, *Inorg. Chem.*, *9*, 1053 (1970).
(b) R.F. Fenske and M.B. Hall, *ibid.*, *11*, 1619 (1972).

ε is the dielectric constant of the medium [17] is shown in Figure 3. The $A_1^{(1)}$ and B_2 modes (Figure 3(a)) which represent the stretching of the equatorial (*trans* to the diketone) CO groups increase markedly in frequency with increasing solvent polarity, whilst the $A_1^{(2)}$ and B_1 modes of the axial groups exhibit the

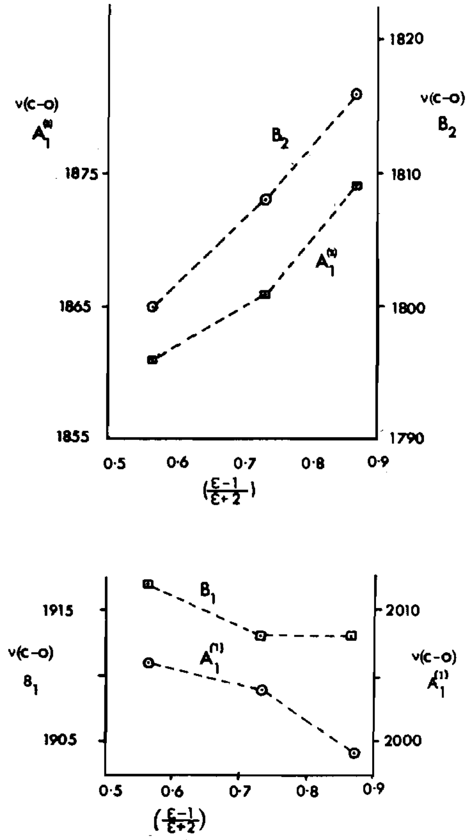

Figure 3. Carbonyl stretching frequency [ν(C-O)] versus (ε—1/ε+2) for $Mo(CO)_4ttaS^-$. (a) $A_1^{(2)}$□ and B_2○ modes-cm^{-1}. (b) $A_1^{(1)}$○ and B_1□ modes-cm^{-1}.

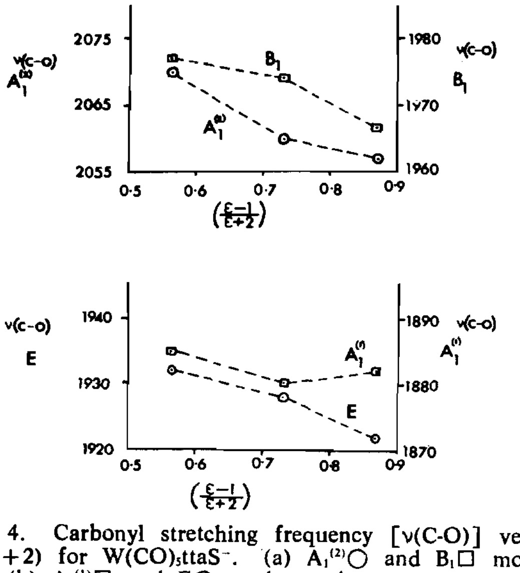

Figure 4. Carbonyl stretching frequency [ν(C-O)] versus (ε—1/ε+2) for $W(CO)_5ttaS^-$. (a) $A_1^{(2)}$○ and B_1□ modes-cm^{-1}. (b) $A_1^{(1)}$□ and E○ modes-cm^{-1}.

(17) "The Handbook of Physics and Chemistry" Ed. R.C. Weast, The Chemical Rubber Co. 1971.

expected decrease in frequency with increasing solvation.[12] These results are typical of all the tetracarbonyl complexes.

A similar plot for the pentacarbonyl complex $W(CO)_5ttaS^-$ (Figure 4) shows a decrease in the $A_1^{(2)}$, B_1 and E modes with increasing polarity of the solvent, whilst the $A_1^{(1)}$ mode representing the trans CO group remains virtually unchanged. The Cr and Mo complexes exhibit similar changes.

The phenomenon of increasing stretching frequency with increasing solvent polarity has been reported for nitrosyl chloride,[12a] some metal carbonyl halides[18] and $Mo(CO)_4$bipy,[13] and has been explained in the case of the carbonyl halides by assuming specific solvation of the metal-halogen bond.[18] It has been suggested that the more polar solvents augment the M–$\overset{\delta+}{C}$–$\overset{\delta-}{O}$ dipole[19] thereby decreasing the C–O bond strength and perhaps increasing the M–C bond strength. Recent evidence[20] based on reactivity of the carbonyl carbon shows that lowering of the C–O bond strength by increased π-back-donation tends to neutralise the positive charge on the carbon atom. This suggests that the dipole which is being solvated is $\overset{\delta+}{M}$–C–$\overset{\delta-}{O}$ and thus solvent interactions will take place mainly at the $O^{\delta-}$. The effect should still decrease the C–O bond strength.

In $Mo(CO)_4ttaS^-$ this is observed only in the axial CO groups. Although it presumably operates in the equatorial CO groups as well, the changing polarity of the $\overset{\delta+}{M}$–$\overset{\delta-}{S}$ and $\overset{\delta+}{M}$–$\overset{\delta-}{O}$ bonds with increased solvent polarity is the dominant effect. Since the diketone has a formal negative charge increased solvation should stabilise this charge on the ligand and thus make it a poorer σ donor. This would result in a decrease in the M–C bond strength of the equatorial CO groups and would adequately explain the trends shown in Figure 3(a).

In the pentacarbonyl complexes the constancy of the $A_1{}^1$ vibration probably results from a similar effect, the decrease due to solvation of $\overset{\delta+}{M}$–C–$\overset{\delta-}{O}$ being offset by the solvation of the $\overset{\delta+}{M}$–$\overset{\delta-}{S}$ bond. Further support for this rationale is to be found in the solvent dependence of the carbonyl stretching frequencies of $Cr(CO)_5$ piperidine.[21] In this case the $A_1{}^1$ vibration does decrease with increasing solvent polarity since the $\overset{\delta+}{M}$–C–$\overset{\delta-}{O}$ solvent interaction now dominates any effect due to the solvation of the piperidine moiety.

It thus seems clear that solvent shifts in substituted metal carbonyls depend not only on solvation of the $\overset{\delta+}{M}$–C–$\overset{\delta-}{O}$ groups but also on the charge distribution over the substituent ligands.

Bonding. The presence of a sulphur donor in the monothio-β-diketone ttaS, introduces the possibility

(18) L.A.W. Hales and R.J. Irving, *Spectrochim Acta (A)*, *23*, 2981 (1967).
(19) L.M. Haines and M.H.B. Stiddard, *Adv. in Inorg. and Radiochem.*, *12*, 53 (1969).
(20) D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem.*, *9*, 1691 (1970).
(21) R.J. Dennenberg and D.J. Darensbourg, *Inorg. Chem.*, *11*, 72 (1972).

of metal to sulphur $d\pi$–$d\pi$ back-bonding which cannot occur in the oxygen analogue tta. In the carbonyl complexes of these ligands, ttaS might be expected to give rise to higher values of the carbonyl stretching force constants k_1 and k_2[6] than tta, due to M–S π bonding. However tta (pK_a 8.64)[1b] is a stronger σ donor than ttaS (pK_a 7.05)[1b] and this should also lead to the high values of k_1 and k_2 for the ttaS complexes, as shown in Table III.

A comparison of the values of these constants for $M(CO)_4ttaS^-$ with those for $M(CO)_4tta^-$ (Table VII) shows that $\Delta k_1 > \Delta k_2$ as expected on the basis of simple π bonding arguments. Isotropic σ bonding differences would influence the axial and equatorial carbonyls equally, whereas the greater degree of "direct donation"[16] from the σ orbitals of ttaS into the π^* of the remaining CO groups would be expected to affect k_2 more than k_1. The possibility of "direct donation" cannot be ruled out but of the two anisotropic effects π bonding must be greater in magnitude.

The relative positions of the M–C stretching modes in the tetracarbonyls (Table VII) provide some evidence for a component of "direct donation" between ttaS and the CO groups.[15] The observed increase in the M–C stretching frequencies of $M(CO)_4ttaS^-$ relative to $M(CO)_4tta^-$ is in agreement with ttaS being a stronger "direct donor" than tta.[15] Although π bonding alone would have the opposite effect, we cannot rule out the possibility that coupling with other modes *e.g.*, δ(M–C–O) might account for the relative positions of ν(M–C).

Two qualitative methods have been proposed for evaluating the σ and π contributions to the metal-ligand bond in the pentacarbonyl complexes, $M(CO)_5L$. Graham[22] has suggested the following relationships,

$$\Delta k_1 = \Delta\sigma + 2\Delta\pi \quad (1)$$

$$\Delta k_2 = \Delta\sigma + \Delta\pi \quad (2)$$

A recent modification of these which eliminates σ effects has been put forward by Brown and Dobson[15] and is based on the concept of "direct donation". They suggest

$$\Delta k_1 = 2\Delta\pi \quad (3)$$

$$\Delta k_2 = \Delta d + \Delta\pi \quad (4)$$

(where Δd is the change in « direct donation »).

We have calculated the π contribution to the bonding of ttaS in $W(CO)_5ttaS^-$ using both these approaches (Table IX). For comparison we have also examined the carbonyl stretching force constants (from data obtained in CH_2Cl_2 solution) of a series of complexes $W(CO)_5RCO_2^-$[23] for which π bonding should be negligible. In these calculations the complex $W(CO)_5HCO_2^-$ has been used as a reference. The Graham σ and π parameters indicate that the carboxylates are weak σ donors and good π donors, whereas the method of Brown and Dobson shows that these anions have negligible π effects and are in general poor "direct donors". Although the values of the Graham σ parameters fit the expected gradation in σ abilities of the oxygen ligands we favour the conclusions based on the Brown-Dobson method. Molecular orbital calculations by Fenske[16] for metal carbonyl halide complexes have shown that although the Graham parameters indicate that the halide ions are π donors,[22] the trends in the parameters are best explained by invoking "direct donation" from the halogen to the *cis* CO groups.

With regard to ttaS, the Brown-Dobson parameters show that relative to the formate ion, the monothio-β-diketone acts as a strong π acceptor. As a "direct donor" it is also marginally better than formate ion and very much better than the fluorinated carboxylates. We have confirmed these properties in a number of other monothio-β-diketone complexes.[14]

(22) W.A.G. Graham, *Inorg Chem.*, 7, 315 (1968).
(23) W.J.Schlientz, Y. Lavender, N. Welcman, R.B. King and J.K.Ruff, *J. Organometal. Chem.*, 33, 357 (1971).

Table VIII. Values of k_1 and k_2 for $M(CO)_4ttaS^-$ relative to $M(CO)_4tta^-$ (m-dyne/Å).

Metal	Δk_1	Δk_2
Cr	0.22	0.16
Mo	0.21	0.14
W	0.21	0.17

Conclusions

From the infrared and nmr spectra of the tetracarbonyl and pentacarbonyl complexes of ttaS we have obtained evidence for both π bonding and "direct donation" between the metal and the monothio-β-diketone. In general sulphur is a better "direct donor" than oxygen which is to be expected since the σ orbital of sulphur is larger and less directional than that of oxygen. We suggest that M–S back bonding is responsible for the differences between the nmr spectra of $W(CO)_4ttaS^-$ and $W(CO)_4tta^-$ and this is substantiated by the large positive π parameter calculated from the infrared data for $W(CO)_5ttaS^-$.

The infrared data for all the complexes were obtained from dichloromethane solutions and in view of the predictable solvent dependence of these data, the results are reasonably self-consistent. However, comparison of the complex $Cr(CO)_5$piperidine[21] with the carboxylate complexes (Table IX) results in ridiculous values of the π parameter, even though the same solvent was employed in both cases. It should be noted that the piperidine and carboxylate complexes are neutral and anionic respectively and we believe that self-consistent results can only be obtained by comparing complexes of the same charge.

Experimental Section

Thenoyltrifluoroacetone (tta) and chromium hexacarbonyl were obtained from Fluka A.G. Buchs S.G. Molybdenum and tungsten hexacarbonyls were obtained from B.D.H. The solvents were purified and dried by conventional methods.[24]

(24) D.D. Perrin, W.L.F. Armarego and D.R. Perrin, "Purification of Laboratory Solvents" Pergamon (1966).

Table IX. (i) $\Delta\sigma$ and $\Delta\pi$ parameters of $W(CO)_5L$ relative to $W(CO)_5HCO_2^-$.*

Ligand	k_1 [c]	k_2 [c]	$\Delta\sigma$ [a]	$\Delta\pi$ [a]	Δd [b]	$\Delta\pi$ [b]
HCO_2^-	13.89	15.50	—	—	—	—
$CH_3CO_2^-$	13.83	15.56	+0.06	—0.12	+0.09	—0.03
$C_2H_5CO_2^-$	13.98	15.68	+0.27	—0.09	+0.13	+0.05
$C_6H_5CO_2^-$	13.80	15.58	+0.25	—0.17	+0.13	—0.05
$CF_3CO_2^-$	13.96	15.71	+0.35	—0.14	+0.17	+0.04
$C_2F_5CO_2^-$	13.85	15.64	+0.32	—0.18	+0.18	—0.02
$C_6F_5CO_2^-$	13.94	15.70	+0.35	—0.15	+0.17	+0.03
$ttaS^-$	14.49	15.76	—0.08	+0.34	—0.04	+0.30
(ii) $Cr(CO)_5L$ relative to $Cr(CO)_5CF_3CO_2^-$.						
$CF_3CO_2^-$	13.92	15.71	—	—	—	—
$ttaS^-$	14.49	15.77	—0.47	+0.52	—0.24	+0.29
piperidine	14.61	15.69	—0.73	+0.71	—0.37	+0.35

[a] Graham $\Delta\sigma$ and $\Delta\pi$.[22] [b] Brown-Dobson Δd and $\Delta\pi$.[15] [c] Calculated by the Cotton-Kraihanzel method.[6] * Positive values of $\Delta\sigma$, $\Delta\pi$ and Δd indicate that the ligands are better *acceptors* than the reference. Negative values imply that the ligands are better *donors*.[15,22]

Infrared spectra in the region 4000-250 cm^{-1} were recorded on a Perkin-Elmer 457 Grating Infrared Spectrometer in Nujol mulls on CsI plates and in solution in KBr cells (0.1 mm). Above 600 cm^{-1} polystyrene peaks were used to calibrate the instrument. The calibrant below 600 cm^{-1} was indene. Frequencies are believed to be accurate to ± 1 cm^{-1}.

The nmr spectra of both the ligands and the complexes in tetrahydrofuran solution were run on a Varian A60 Spectrometer.

Conductivity of the complexes *ca.* $10^{-4}M$ in THF were measured with a Mullard conductivity bridge and dip-type bright platinum electrodes.

Microanalyses (Table I) were performed by the C.S.I.R.O. Microanalytical Service, Melbourne (Australia) and Alfred Bernhardt, Microanalytical Laboratories, Elbach (W. Germany).

The complexes $NEt_4[M(CO)_5Cl]$ were made under nitrogen by the method of Abel, Butler and Reid,[25] the ligand ttaS was prepared as described by Livingstone et al. [1(a)] and the thallium complexes Tl(tta) and Tl(ttaS) by the procedure of Hartmann, Kilner and Wojcicki.[2b] Other preparations were carried out in an inert atmosphere (N_2) dry box, as follows.

Pentacarbonyl complexes of monothiothenoyltrifluoroacetone. TlttaS (0.4 g: 1.0 mmole) in diglyme (10 ml) was added to a solution of $NEt_4[W(CO)_5Cl]$ (0.4 g; 0.9 mmole) in diglyme (10 ml). The solution rapidly turned deep orange-red and a precipitate formed. After stirring for 10 minutes the solution was filtered through microcrystalline cellulose and petroleum ether (50 ml) was added slowly to the filtrate with stirring. Red needle-like crystals rapidly formed and were filtered off and washed succesively with diisopropyl ether and petroleum ether then dried by suction. Yield 0.5 g.

The molybdenum and chromium complexes were prepared similarly but in ethanol and with the reaction period reduced to 5 minutes to inhibit the formation of the tetracarbonyl complexes.

Yield of $NEt_4[Mo(CO)_5ttaS]$	0.1 g
Yield of $NEt_4[Cr(CO)_5ttaS]$	0.2 g

Tetracarbonyl complexes of tta and ttaS. These were prepared by the same method as that used for the pentacarbonyls but in diglyme at 60-80°. Addition of petroleum ether tc the filtrate produced an oil which was dissolved in a minimum volume of ethanol. Cautions addition, with stirring, of diisopropyl ether and finally petroleum ether gave intensely coloured crystals of the product. Yield 0.2 to 0.4 g.

Tricarbonyl complexes. The tetracarbonyl complexes prepared as above were treated with a twofold excess of triphenylphosphine in tetrahydrofuran at 40°. The solutions changed colour and after 10-15 minutes were filtered through microcrystalline cellulose. Diisopropyl ether was added slowly with stirring to the filtrate, giving crystals of the tricarbonyl complexes, which were filtered off and washed thoroughly with diisopropyl ether and petroleum ether.

Molecular weight of $NEt_4[W(CO)_5ttaS]$. The space group and unit cell dimensions of the complex were determined by standard-X-ray photographic techniques on a single crystal. From these data and the density of the crystals the molecular weight was calculated to be 708. The theoretical value for $N(C_2H_5)_4$-$[W(CO)_5C_8H_4F_3S_2O]$ is 691.39.

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(25) E.W. Abel, I.S. Butler and J.G. Reid, *J. Chem. Soc.*, 2068 (1963).