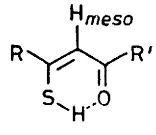
Unidentate Sulphur-bonded Monothio-β-diketone Complexes of Chromium(0), Molybdenum(0), and Tungsten(0) and their Protonation. The *X*-Ray Structure Analysis of Tetraethylammonium Pentacarbonyl[1,1,1-trifluoro-4-(2-thienyl)-4-thioxobutan-2-onato-*S*]tungstate(0)

By **George H. Barnett** and **Mervyn K. Cooper**,* School of Chemistry, The University of Sydney, Sydney 2006, Australia
Mary McPartlin *,† and **Glen B. Robertson**, Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia

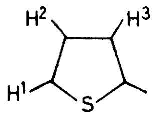
The syntheses of the tetraethylammonium salts of the complex anions $[M(CO)_5L]^-$ [M = Cr, Mo, or W; L = mono-β-diketonate anions RCSCHOCR' (R = CF_3 or thienyl, R' = CF_3); R = Me, R' = CF_3, Me, or Ph; R = R' = Ph)] are reported. Hydrogen-1 n.m.r. and i.r. data show that the monothio-β-diketonate ligand is unidentate and co-ordinated through the sulphur atom. A single-crystal *X*-ray structure analysis has shown that in the title complex the *S*-bonded unidentate ligand is present in a hitherto unobserved *trans* configuration. The complex crystallises in space group $C222_1$ with a = 8.818(5), b = 18.615(10), and c = 31.992(18) Å. Block-diagonal least-squares refinement of 2 559 reflections collected with a four-circle diffractometer has converged to R 0.038. The W–S bond length is 2.543(2) Å. Protonation of the $[M(CO)_5L]^-$ species gives a series of highly unstable neutral complexes $[M(CO)_5(HL)]$. Hydrogen-1 n.m.r. and i.r. data show that in these complexes the *S*-bonded unidentate ligand is in a *cis* conformation similar to that of the free protonated ligand.

RECENTLY we reported the preparation and characterisation of substituted metal carbonyl complexes of the β-diketone 1,1,1-trifluoro-4-(2-thienyl)butane-2,4-dione and its monothio-derivatives with Group 6A metals in the zero oxidation state. Two series of complexes with the monothio-derivative HL^2 were isolated, $[M(CO)_5L^2]^-$ and $[M(CO)_4L^2]^-$ (M = Cr, Mo, or W).[1,2] In the pentacarbonyls the monothio-β-diketone acts as a unidentate sulphur donor whereas in the tetracarbonyls it behaves as a bidentate sulphur–oxygen chelating agent. A preliminary single-crystal *X*-ray structure analysis of one of these complexes, tetraethylammonium pentacarbonyl[1,1,1-trifluoro-4-(2-thienyl)-4-thioxobutan-2-onato-*S*]tungstate(0), showed that when the monothio-β-diketone acts as a unidentate ligand it adopts the unusual *trans* configuration.[3] The details of this structure are reported here, together with the synthesis and characterisation of a series of analogous complexes $[M(CO)_5L]^-$ and the neutral complexes formed when they react with strong acids.



HL

L	R	R'
L^1	CF_3	CF_3
L^2	thienyl	CF_3
L^3	Me	CF_3
L^4	Me	Me
L^5	Me	Ph
L^6	Ph	Ph



R = thienyl

EXPERIMENTAL

Materials.—Chromium hexacarbonyl and the β-diketones 1,1,1,5,5,5-hexafluoropentane-2,4-dione, 1,1,1-trifluoro-4-(2-thienyl)butane-2,4-dione, 1,1,1-trifluoropentane-2,4-dione, 4-phenylbutane-2,4-dione, and 1,3-diphenylpropane-1,3-dione were obtained from Fluka A.G. Buchs S.G.,

---

† *Present address:* Department of Chemistry, The Polytechnic of North London, London N7 8DB.

[1] G. H. Barnett and M. K. Cooper, *Chem. Comm.*, 1971, 1082.

[2] G. H. Barnett and M. K. Cooper, *Inorg. Chim. Acta*, 1973, **7**, 613.

[3] M. McPartlin, G. B. Robertson, G. H. Barnett, and M. K. Cooper, *J.C.S. Chem. Comm.*, 1974, 305.

pentane-2,4-dione was purchased from Ajax Chemicals, and 1,1,1,5,5,5-hexafluoro-4-thioxopentan-2-one (HL^1) from Pierce Chemicals. Molybdenum and tungsten hexacarbonyls were donated by the Climax Molybdenum Co. The solvents used were purified and dried by conventional means and stored under nitrogen.[4]

The intermediates $[NEt_4][M(CO)_5Cl]$ were prepared by published methods[5] as were the monothio-β-diketones, 1,1,1-trifluoro-4-(2-thienyl)-4-thioxobutan-2-one (HL^2), 1,1,1-trifluoro-4-thioxopentan-2-one (HL^3), 4-thioxopentan-2-one (HL^4), 4-phenyl-2-thioxobutan-4-one (HL^5), and 1,3-diphenyl-3-thioxopropan-1-one (HL^6).[6] Thallium(I) derivatives of the monothio-β-diketones (TlL) were made by modifying the procedures of Hartmann *et al.*[7] and Lee.[8] The salt TlL^4 was made in ethanol[8] but soluble thallium ethoxide was substituted for thallium hydroxide. For the other TlL derivatives, enhanced yields and higher purity were obtained by replacing the solvent chloroform[7] by tetrahydrofuran (thf) in which they were more soluble.

All the other preparations described below were carried out in an inert-atmosphere glove-box.

Preparations.—*Pentacarbonyl(monothio-β-diketonato)-metallate*(0) *complexes.* For the tungsten complexes, TlL (1.0 mmol) in diglyme or thf (10 cm^3) was added to a solution of $[NEt_4][W(CO)_5Cl]$ (0.9 mmol) in diglyme or thf (10 cm^3). The solution rapidly darkened and a precipitate formed. After stirring for 10—15 min the mixture was filtered through microcrystalline cellulose and light petroleum (5 cm^3) was added slowly to the filtrate with stirring. If crystals formed they were filtered off, washed successively with di-isopropyl ether and light petroleum, then dried by suction. However, if an oil formed at this point the product was dissolved in ethanol and carefully reprecipitated with di-isopropyl ether followed by light petroleum. The chromium and molybdenum complexes were prepared by a similar method in ethanol with the reaction period reduced to 5 min to prevent extensive formation of the tetracarbonyls. Analytical figures for some of the more stable representative complexes are listed in Table 1.

TABLE 1

Properties of the pentacarbonyl(monothio-β-diketonato) complexes [a]

Complex [b]	Colour	Λ [c] S cm^2 mol^{-1}	Analysis (%) [d] C	H	N	F	S	M
$[NEt_4][Cr(CO)_5L^2]$	Deep red	117	44.9 (45.1)	4.40 (4.30)		9.7 (10.2)	11.1 (11.5)	9.4 (9.5)
$[NEt_4][Cr(CO)_5L^6]$	Orange		59.7 (59.8)	6.20 (5.75)	2.80 (2.50)		5.2 (5.7)	
$[NEt_4][Mo(CO)_5L^2]$	Deep red	118	41.25 (41.7)	4.05 (3.95)		9.0 (9.4)	9.4 (10.6)	23.4 (23.9)
$[NEt_4][W(CO)_5L^1]$	Deep red		31.5 (31.95)	3.15 (3.15)	2.05 (2.05)	16.2 (16.8)	3.8 (4.7)	
$[NEt_4][W(CO)_5L^2]$	Deep red	114	36.45 (36.5)	3.75 (3.50)	2.45 (2.05)		8.9 (9.3)	27.0 (26.6)
$[NEt_4][W(CO)_5L^3]$	Orange		34.4 (34.7)	3.75 (3.90)	2.00 (2.25)		5.2 (5.1)	
$[NEt_4][W(CO)_5L^4]$	Orange-brown		37.85 (37.95)	4.35 (4.80)	2.40 (2.45)			42.5 (40.7)
$[NEt_4][W(CO)_5L^5]$	Orange		43.85 (43.75)	4.70 (4.60)	2.20 (2.20)		5.2 (5.1)	
$[NEt_4][W(CO)_5L^6]$	Orange		47.6 (48.5)	4.40 (4.65)	1.80 (2.00)		4.6 (4.6)	

[a] The pentacarbonyls not listed were identified by comparison of their i.r. spectra with those of the complexes in this Table. [b] The complexes are crystalline solids at room temperature. [c] For *ca.* 10^{-4} mol dm^{-3} solutions of the complexes in thf. [d] Numbers in parentheses are calculated values.

Protonated pentacarbonyl(monothio-β-diketonato)metal(0) *complexes.* The monothio-β-diketone complexes of tungsten and chromium, $[M(CO)_5L]^-$ (0.2 mmol), prepared as described above were dissolved in a minimum volume of dichloromethane or chloroform and two drops (*ca.* 0.6 mmol) of 6 mol dm^{-3} sulphuric acid were added. The mixture was shaken, at which point the mixture darkened in colour. Filtration through phase-separating filter paper and evaporation of the solvent gave the dark oily products $[Cr(CO)_5(HL^2)]$ (green), $[Cr(CO)_5(HL^6)]$ (green), $[W(CO)_5(HL^2)]$ (blue), $[W(CO)_5(HL^3)]$ (purple), $[W(CO)_5(HL^4)]$ (pink), $[W(CO)_5(HL^5)]$ (purple), and $[W(CO)_5(HL^6)]$ (blue). These neutral complexes had limited stability under both nitrogen and carbon monoxide and no satisfactory analyses could be obtained.

Apparatus and Techniques.—Infrared spectra were recorded on a Perkin-Elmer 457 grating i.r. spectrometer for Nujol mulls on CsI plates and for solutions in KBr cells (0.1, 1 mm). Polystyrene peaks were used to calibrate the instrument to ± 1 cm^{-1} unless otherwise stated. The n.m.r. spectra of both the ligands and the complexes in thf, deuteriochloroform, or carbon tetrachloride were run on a Varian A60 spectrometer with tetramethylsilane as internal standard. Microanalyses were by the C.S.I.R.O. Microanalytical Service, Melbourne, Australia, or Alfred Bernhardt Microanalytical Laboratories, Elbach, West Germany.

Crystal Data.—$C_{21}H_{24}F_3NO_6S_2W$, $M = 691.4$, Orthorhombic, space group $C222_1$, $a = 8.818(5)$, $b = 18.615(10)$, $c = 31.992(18)$ Å, $D_m = 1.69$ g cm^{-3}, $Z = 8$, $D_c = 1.71$ g cm^{-3}, $F(000) = 2\,272$, Cu-K_α radiation, $\mu = 102.5$ cm^{-1}.

The crystal chosen for data collection, of dimensions $0.03 \times 0.01 \times 0.01$ cm (elongated in the *a* direction), was aligned on a Picker FACS-I automatic diffractometer with the crystallographic *a* and the machine ϕ axes approximately coincident. Cell dimensions and the crystal-orientation matrix, together with estimated standard errors, were obtained in the usual way from least-squares refinement of the 2θ, ω, χ, and ϕ values of 12 carefully centred high-angle reflections.

Data Collection.—Reflections of the form *hkl* within the range $3 \leqslant 2\theta \leqslant 127°$ were recorded by the θ—2θ scan technique, with a 2θ velocity of 2° min^{-1} and an asymmetric scan range from $(2\theta - 0.85)°$ to $(2\theta + 0.85 + \Delta)°$, where Δ is the angular separation between the α_1 and α_2 components of the reflection concerned. Backgrounds were counted for 10 s at the scan-range limits and were assumed to be

---

[4] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Solvents,' Pergamon, Oxford, 1966.

[5] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 1963, 2068.

[6] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Austral. J. Chem.*, 1965, **18**, 673.

[7] F. Hartmann, M. Kilner, and A. Wojcicki, *Inorg. Chem.*, 1967, **6**, 34.

[8] A. G. Lee, *J. Chem. Soc.* (*A*), 1971, 2007.

linear between these two points. The intensities of three reflections distributed nearly orthogonally in reciprocal space and at 2θ *ca.* 50—60° were monitored after every 60 measurements. None showed a significant intensity variation during data collection. Graphite-crystal-monochromated Cu-K_α radiation was used throughout.

The method of data reduction and the estimation of the individual standard deviations were as described previously,[9] and gave 2 559 unique reflections with $I/\sigma(I) > 3.0$.

Solution and Refinement.—The co-ordinates of all the atoms, except hydrogen and fluorine, were readily obtained by conventional Patterson and Fourier syntheses. Initial block-diagonal least-squares refinement of these atomic co-ordinates with individual isotropic temperature factors gave R 0.117. A difference-Fourier synthesis, calculated at this stage, revealed two arcs of electron density spanning a range of possible positions for the fluorine atoms and indicating restricted rotation of the CF_3 group. No program was available which could accurately take account of this behaviour. However, close examination of the electron-density distribution showed six local maxima which suggested that there were two preferred orientations for the CF_3 group. Fluorine atoms, each with an occupation factor of 0.5, were allocated to these six positions, and they were included in later isotropic refinements giving R 0.098.

TABLE 2

Fractional co-ordinates for $[NEt_4][W(CO)_5L^2]$ with estimated standard deviations in parentheses

Atom	x	y	z
W	0.161 29(5)	0.151 48(2)	0.039 42(1)
S(1)	0.144 77(32)	0.032 20(11)	0.077 90(7)
S(2)	0.193 54(43)	−0.113 59(14)	0.118 21(11)
O(1)	−0.097 3(9)	0.088 8(5)	−0.019 5(3)
O(2)	0.404 1(10)	0.086 9(6)	−0.023 4(3)
O(3)	0.437 4(10)	0.212 3(5)	0.092 3(3)
O(4)	−0.087 4(11)	0.227 6(5)	0.096 3(3)
O(5)	0.171 4(13)	0.291 0(4)	−0.014 3(3)
O(6)	0.272 7(18)	0.068 0(5)	0.221 9(3)
N	0.326 7(9)	−0.010 9(4)	0.363 1(2)
C(1)	−0.007 4(14)	0.111 4(5)	0.001 8(3)
C(2)	0.316 7(13)	0.108 5(6)	−0.000 8(3)
C(3)	0.336 3(14)	0.190 4(5)	0.074 3(3)
C(4)	0.002 4(14)	0.198 9(6)	0.076 2(3)
C(5)	0.168 6(12)	0.239 7(6)	0.005 7(3)
C(6)	0.237 3(21)	0.190 6(9)	0.208 4(4)
C(7)	0.229 3(16)	0.110 6(5)	0.194 3(3)
C(8)	0.186 8(13)	0.095 8(5)	0.152 9(3)
C(9)	0.170 1(11)	0.032 9(4)	0.131 5(3)
C(10)	0.166 7(12)	−0.040 3(5)	0.149 4(3)
C(11)	0.131 5(12)	−0.060 6(5)	0.192 4(3)
C(12)	0.132 2(16)	−0.137 1(7)	0.194 8(4)
C(13)	0.165 8(19)	−0.169 2(6)	0.158 0(5)
C(14)	0.430 9(16)	−0.040 1(9)	0.329 3(4)
C(15)	0.343 2(23)	−0.074 6(10)	0.291 9(4)
C(16)	0.226 0(14)	0.048 8(6)	0.346 6(4)
C(17)	0.311 1(22)	0.114 3(7)	0.329 5(4)
C(18)	0.433 2(14)	0.018 3(6)	0.397 1(3)
C(19)	0.346 4(19)	0.049 6(7)	0.434 8(3)
C(20)	0.221 3(13)	−0.068 3(5)	0.380 1(4)
C(21)	0.299 5(20)	−0.134 5(6)	0.398 6(4)
F(1A)	0.164 9	0.232 7	0.184 3
F(1B)	0.087 8	0.218 3	0.197 5
F(2A)	0.395 2	0.208 8	0.203 4
F(2B)	0.291 4	0.231 2	0.179 6
F(3A)	0.186 6	0.203 5	0.242 8
F(3B)	0.292 7	0.202 2	0.242 9

At this point the data were corrected for absorption effects by the use of 18 × 6 × 6 grid in the *a*, *b*, and *c* directions. Further refinement of the overall scale factor, individual atom co-ordinates, and isotropic thermal parameters reduced R to 0.074. Introduction of anisotropic temperature factors for all the atoms except fluorine (which were not refined further) reduced R to 0.042.

Comparison of observed and calculated structure factors showed that a few of the strongest reflections had low F_o values, possibly due to extinction effects. These were excluded in the final block-diagonal least-squares refinement cycles, in which individual weights $[w = 1/\sigma^2(F_o)]$ were used, which converged to R 0.038 (R' 0.047). A final difference Fourier revealed diffuse peaks having *ca.* 0.5e Å^{-3} and corresponding to the hydrogen atoms which were not included in the refinement. There were no peaks higher than 0.5e Å^{-3} in the region around the fluorine atoms showing that the model used was reasonable.

The atomic scattering factors were those of Cromer and Mann,[10] and those of tungsten and sulphur were corrected for both real and imaginary anomalous-scattering contributions. Reversing the sign of the imaginary anomalous-scattering contributions resulted in a significant increase in the final R to 0.053. The model therefore has the correct absolute configuration.

Supplementary Publication No. SUP 22227 (17 pp.) * contains observed and calculated structure factors, thermal parameters, bond lengths, interbond angles, non-bonded contacts of less than 3.5 Å, and details of least-squares planes. Table 2 lists the final atomic co-ordinates.

RESULTS AND DISCUSSION

Reaction of the thallium(I) complexes TlL (L = L^1—L^6) with the pentacarbonylchlorometallate(0) ions $[M(CO)_5Cl]^-$ (M = Cr, Mo, or W) at room temperature produces the orange to red diamagnetic anions $[M(CO)_5L]^-$ which can be isolated as their tetraethylammonium salts. In general, when the chromium or tungsten complexes $[M(CO)_5L]^-$ are dissolved in CH_2Cl_2 or $CHCl_3$ containing a little trifluoroacetic or sulphuric acid the highly unstable diamagnetic complexes $[M(CO)_5(HL)]$ (M = Cr or W) are rapidly formed. The complexes $[Cr(CO)_5L^1]^-$ and $[W(CO)_5L^1]^-$ are exceptional in this regard, decomposing instantly in the presence of acids as do all the analogous molybdenum complexes, $[Mo(CO)_5L]^-$. No transient protonated species are observed in the course of decomposition. The tetracarbonyl chelates $[M(CO)_4L]^-$ (L = β-diketonate or monothio-β-diketonate) are also decomposed apparently without protonation.

The carbonyl-stretching frequencies of the pentacarbonyl complexes are shown in Table 3. The number, position, and relative intensity of the non-ketonic bands are characteristic of octahedral $[M(CO)_5L]$ complexes having pseudo-C_{4v} symmetry.[11,12] We have assigned the modes on the basis of force-constant analysis (Table

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[9] G. B. Robertson and P. O. Whimp, *J.C.S. Dalton*, 1973, 2454.

[10] D. J. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[11] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[12] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

3) using the method of Cotton and Kraihanzel.[13] Table 4 lists the ketonic stretching frequencies for the anionic pentacarbonyl complexes together with the corresponding values for the free ligands and the bidentate $[M(CO)_4L]^-$ species.[14] For the $[M(CO)_5L]^-$ complexes this band occurs at higher frequency than in the free ligand which for these ligands is diagnostic of unidentate *S*-co-ordination.[1,2] On the other hand, for the bidentate tetracarbonyl complexes this band occurs at lower frequency than in the free ligand, consistent with electron delocalisation in the chelate ring.

TABLE 3

Terminal carbonyl stretching frequencies (cm^{-1}), relative intensities,[a] assignments, and force constants (mdyn Å^{-1}) [b] for the pentacarbonyl complexes

Ligand	$A_1^{(1)}$ (w)	B_1 (w)	E (s)	$A_1^{(2)}$ (ms)	k_1	k_2	k_i
(*a*) $[Cr(CO)_5L]^-$ [c]							
L^1	2 056	1 974	1 932	1 895	14.73	15.77	0.36
L^2	2 054	1 971	1 926	1 890	14.65	15.71	0.37
L^3	2 054	1 970	1 929	1 887	14.59	15.72	0.36
L^4	2 044	1 967	1 921	1 880	14.48	15.62	0.35
L^5	2 045	1 965	1 921	1 883	14.54	15.61	0.36
L^6	2 049	1 966	1 923	1 880	14.49	15.63	0.36
(*b*) $[Cr(CO)_5(HL)]$ [d]							
HL^2	2 068	2 001	1 961	1 957	15.70	16.14	0.30
HL^6	2 065		1 958	1 943	15.47	16.09	0.31
(*c*) $[Mo(CO)_5L]^-$ [c]							
L^1	2 061	1 975	1 938	1 890	14.63	15.83	0.36
L^2	2 060	1 973	1 937	1 880	14.47	15.81	0.36
L^3	2 065	1 972	1 930	1 883	14.55	15.78	0.39
L^4	2 055	1 969	1 926	1 874	14.39	15.70	0.37
L^5	2 056	1 968	1 925	1 873	14.38	15.69	0.38
L^6	2 056	1 972	1 924	1 871	14.35	15.71	0.38
(*d*) $[W(CO)_5L]^-$ [c]							
L^1	2 063	1 972	1 929	1 890	14.68	15.76	0.39
L^2	2 060	1 966	1 929	1 880	14.51	15.72	0.38
L^3	2 058	1 967	1 923	1 889	14.66	15.78	0.39
L^4	2 057	1 963	1 918	1 874	14.43	15.62	0.40
L^5	2 056	1 963	1 921	1 874	14.42	15.62	0.39
L^6	2 053	1 961	1 919	1 877	14.46	15.60	0.39
(*e*) $[W(CO)_5(HL)]$ [d]							
HL^2	2 074	1 997	1 956	1 950	15.60	16.06	0.33
HL^3	2 073		1 961	1 952	15.62	16.16	0.32
HL^4	2 071		1 949	1 934	15.35	16.02	0.33
HL^5	2 069		1 950	1 935	15.37	16.04	0.34
HL^6	2 068		1 951	1 935	15.36	16.04	0.33

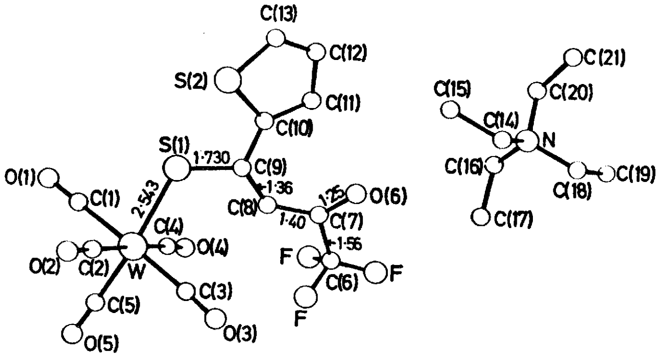
[a] s = Strong, m = medium, and w = weak. [b] Method of Cotton and Kraihanzel.[11] [c] In thf solution. [d] In light petroleum solution.

TABLE 4

Ketonic carbonyl stretching frequencies (cm^{-1}) [a]

L	Free ligand HL	$[M(CO)_5L]^-$ Cr	$[M(CO)_5L]^-$ Mo	$[M(CO)_5L]^-$ W	$[M(CO)_4L]^-$ Cr	$[M(CO)_4L]^-$ Mo	$[M(CO)_4L]^-$ W
(*a*) Unprotonated complexes							
L^1	1 640 [b]	1 671 [c]	1 667 [c]	1 673 [c]	1 627 [c]	1 618 [c]	1 625 [c]
L^2	1 619 [d] 1 623 [e]	1 636 [c]	1 641 [f]	1 640 [c] 1 628 [e]	1 612 [f]	1 598 [c]	1 598 [c]
L^3	1 563 [b]	1 635 [e]	1 635 [c]	1 635 [c]	*g*	1 546 [c]	1 542 [c]
L^4	1 645 [b]	1 640 [c]	1 637 [c]	1 644 [c]	1 612 [c]	1 615 [c]	1 615 [e]
L^5	1 548 [e]	*g*	1 609 [c]	1 612 [e]	*g*	1 518 [c]	1 518 [c]
L^6	1 558 [e]	1 613 [b]	*g*	1 613 [c]	*g*	1 530 [c]	1 521 [c]
(*b*) Protonated complexes							
$[W(CO)_5(HL^2)]$				1 618 [b]			
$[W(CO)_5(HL^5)]$				1 550.0 [b]			

[a] Accurate to ±2 cm^{-1}. [b] Neat liquid. [c] In thf solution. [d] In $CHCl_3$ solution. [e] Nujol mull. [f] In CH_2Cl_2 solution. [g] Not recorded.



The structure of $[NEt_4][W(CO)_5L^2]$

Single-crystal *X*-ray structure analysis of the complex $[NEt_4][W(CO)_5L^2]$ confirms that in the solid state the ligand, L^2, is unidentate and co-ordinated through the thiol sulphur. The crystal structure consists of alternating anionic and cationic groups; neither ion has crystallographic symmetry higher than C_1. The overall structure of these ions, together with the numbering scheme and principal bond lengths, is shown in the Figure. Selected bond lengths and interbond angles are given in Table 5. The tetraethylammonium cation has non-crystallographic C_{2v} symmetry with average bond lengths C–N 1.52(1) and C–C 1.54(2) Å.

The tungsten atom of the complex anion has distorted octahedral co-ordination with bonds from five carbonyl groups and the thiol sulphur atom of a unidentate L^2 ligand as indicated by i.r. data.[2] The main distortions are the S(1)–W–C(1) angle of 85.7(3)° which is significantly less than the angle of 90° expected for regular octahedral geometry and the angles S(1)–W–C(3) [95.1(3)°] and S(1)–W–C(4) [93.4(3)°]. In effect the W–S(1) bond appears to be pushed towards carbonyl(1) in order to minimise the contacts between the L^2 ligand and carbonyl(3); the closest contact is O(3)–F(2b) [3.10(1) Å].

The four tungsten–carbonyl bonds *cis* to the co-ordinated sulphur atom have lengths in the range 2.03—2.05 Å, whereas the *trans* W–C(5) bond length [1.97(1) Å] is significantly shorter. The longer W–C bonds *cis* to S(1) may be attributed to the competition of mutually *trans* carbonyl ligands for π-electron density from the metal. The apparently higher bond order observed for W–C(5) indicates that any π-back bonding from the tungsten to the co-ordinated S(1), in the ***trans*** position, is significantly less than that to the carbonyl ligands. The W–C–O angles (173—179°) are similar to values found for terminal carbonyl groups in other metal complexes; slight deviations from linearity are

---

[13] F. A. Cotton and C. S. Kraihanzel, *Inorg. Chem.*, 1963, **2**, 533.

[14] G. H. Barnett and M. K. Cooper, unpublished work.

common in carbonyl complexes containing an unsymmetrical ligand such as L^2.[15]

Some degree of metal-to-sulphur back bonding was predicted for the unidentate L^2 ligand from the earlier n.m.r. and i.r. studies of this and related complexes.[2] The observed W–S(1) bond length [2.543(2) Å] is shorter than the sum of previously reported covalent radii (2.65 Å) for these atoms.[16] Although the presence of some π character in all the other bonds to the tungsten precludes a direct estimate of the W–S single bond length from internal correlation, the apparent shortening of the W–S(1) bond by 0.11 Å is consistent with considerable double-bond character for this bond. The W–S(1)–C(9) angle [117.8(3)°] is close to the value of 120° expected for sp^2 hybridisation about the sulphur atom. That there is some degree of conjugation, extending from the tungsten atom along the backbone of the ligand, is indicated by the fact that the atoms W, S, C(6), C(7), C(8), C(9), and C(10) are coplanar to within 0.1 Å.

TABLE 5

Selected bond lengths and interbond angles, with estimated standard deviations in parentheses, for the complex $[NEt_4][W(CO)_5L^2]$

(*a*) Bond lengths (Å)

W–S(1)	2.543(2)	S(1)–C(9)	1.730(8)
W–C(1)	2.05(1)	S(2)–C(10)	1.707(10)
W–C(2)	2.04(1)	S(2)–C(13)	1.660(14)
W–C(3)	2.04(1)		
W–C(4)	2.03(1)	C(6)–C(7)	1.56(2)
W–C(5)	1.97(1)	C(7)–C(8)	1.40(1)
		C(8)–C(9)	1.36(1)
C(1)–O(1)	1.13(1)	C(9)–C(10)	1.48(1)
C(2)–O(2)	1.13(1)	C(10)–C(11)	1.46(1)
C(3)–O(3)	1.14(1)	C(11)–C(12)	1.43(2)
C(4)–O(4)	1.15(2)	C(12)–C(13)	1.35(2)
C(5)–O(5)	1.15(1)		
		C(7)–O(6)	1.25(1)

(*b*) Angles (°)

S(1)–W–C(1)	85.7(3)	W–C(3)–O(3)	177(1)
S(1)–W–C(2)	90.1(3)	W–C(4)–O(4)	178(1)
S(1)–W–C(3)	95.1(3)	W–C(5)–O(5)	179(1)
S(1)–W–C(4)	93.4(3)		
S(1)–W–C(5)	175.4(3)	C(6)–C(7)–O(6)	113(1)
C(1)–W–C(2)	175.4(4)	C(6)–C(7)–C(8)	118(1)
C(1)–W–C(3)	177.1(4)		
C(1)–W–C(4)	89.9(5)	O(6)–C(7)–C(8)	129(1)
C(1)–W–C(5)	90.3(4)	O(7)–C(8)–C(9)	132(1)
C(2)–W–C(3)	88.6(4)	C(8)–C(9)–C(10)	126(1)
C(2)–W–C(4)	176.0(4)	C(8)–C(9)–S(1)	121.3(7)
C(2)–W–C(5)	87.6(4)	C(10)–C(9)–S(1)	112.0(6)
C(3)–W–C(4)	92.9(4)	C(9)–C(10)–S(2)	120.5(7)
C(3)–W–C(5)	88.8(4)	C(9)–C(10)–C(11)	127(1)
C(4)–W–C(5)	88.7(4)	S(2)–C(10)–C(11)	112.0(7)
		C(10)–C(11)–C(12)	108(1)
W–S(1)–C(9)	117.8(3)	C(11)–C(12)–C(13)	113(1)
W–C(1)–O(1)	173(1)	C(13)–S(2)–C(10)	91.7(6)
W–C(2)–O(2)	178(1)		

It seems probable that the predominant canonical form in the description of the bonding in the unidentate L^2 ligand is (A). This is supported by the larger upfield shift of the n.m.r. resonance of the *meso* proton when the ligand is uni- rather than bi-dentate (Table 6). The bond lengths within the monothio-β-diketone ligand are also consistent with this structure. In particular C(8)–C(9) [1.36(1) Å] is significantly shorter than C(7)–C(8) [1.40(1) Å], the ketonic C(7)–O(6) bond has a length [1.25(1) Å] consistent with a predominantly double bond, and the S(1)–C(9) bond length [1.730(8) Å] indicates that it has considerable single-bond character.

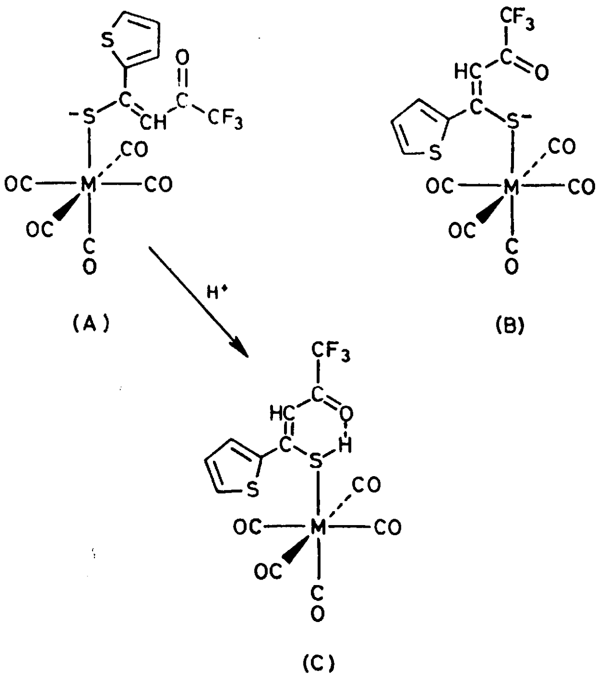


TABLE 6

60-MHz Chemical shifts of *meso* and methyl protons (thf solution, δ in p.p.m. downfield from $SiMe_4$)

	Free ligand, HL		$[W(CO)_5L]^-$		$[W(CO)_5(HL)]$ [a]	
L	$\delta(H_{meso})$	$\delta(CH_3)$	$\delta(H_{meso})$	$\delta(CH_3)$	$\delta(H_{meso})$	$\delta(CH_3)$
L^2	7.17		6.79		7.20	
L^3	6.95	2.83	6.67	2.73	6.76	2.80
L^5	7.19	*b*	6.98	*b*	7.24	*b*

[a] In thf–CF_3CO_2H solution. [b] Not recorded.

The most unusual feature of the structure of the anion is the *trans* configuration of the monothio-β-diketone ligand: the co-ordinated S(1) is *trans* to the carbonyl group C(7)–O(6) about the C(8)–C(9) double bond. Hitherto, in transition-metal complexes all the monothio-β-diketone and β-diketone ligands have been found to adopt the *cis* configuration even when unidentate. The only previous report of a β-diketone type of ligand adopting a *trans* configuration is based on n.m.r. evidence for *cis–trans* equilibrium in solutions of 5-trimethylsilylpentane-2,4-dionate.[17] It appears from calculations, using appropriate bond lengths and angles, that in $[NEt_4][W(CO)_5L^2]$ even the most favourable *cis* configuration (B) of the unidentate L^2 ligand leads to extremely close contacts between the thiophenyl group

---

[15] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1661.

[16] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 157.

[17] J. J. Howe and T. J. Piinnavaia, *J. Amer. Chem. Soc.*, 1969, **91**, 5378.

and the carbonyl ligands. By adopting the *trans* configuration (A) the ligand is able to bond in the unidentate mode with only slight distortions of the angles about the tungsten atom as described above. Assuming that this *trans* form persists in solution, which seems probable on steric grounds, the n.m.r. resonance of H^3 (p. 587) would be deshielded relative to H^1 and H^2 in this configuration (A). Therefore we reassign the resonance at δ 7.79 p.p.m., previously reported[2] as due to H^1 in configuration (B), to H^3 and the resonance at δ 7.43 p.p.m. to H^1. A similar relative deshielding is observed in the methyl group adjacent to the C–S bond in the ligand in $[W(CO)_5L^3]^-$. On co-ordination the methyl (δ 2.73 p.p.m.) is shielded by −0.10 (δ 2.83 p.p.m. in HL^3), whereas H_{meso} is shielded by −0.28 p.p.m. relative to the free ligand (Table 6). This is a strong indication that for this complex in solution the ligand is in a similar *trans* conformation to (A) with the methyl group replacing the thienyl group. Although $[W(CO)_5L^2]^-$ and $[W(CO)_5L^3]^-$ probably have this novel *trans* configuration in solution, n.m.r. and i.r. evidence indicate that the *cis* conformation is adopted by the protonated species. No methylene or metal hydride resonance was observed in the n.m.r. spectra of the protonated complexes, ruling out the possibility that protonation had occurred at the *meso*-carbon or the metal. There is close resemblance between the spectra of the protonated complexes and the free ligands in that the signals of the methyl and *meso*-protons are similar (Table 6). These results suggest that the protonated complex has structure (C). This appears to be confirmed in the case of $[W(CO)_5(HL^2)]$ where the resonance due to the added proton was located well downfield at δ 13.58 p.p.m., very close to the signal of the enolic proton in the free ligand at δ 13.63 p.p.m. This type of unidentate behaviour for a neutral mono-β-diketone ligand has not so far been reported. However, for the protonated β-diketone complex $[\{Re(CO)_3Cl(L)\}_2]$ (L = diketone analogue of L^5) *X*-ray structure analysis and n.m.r. has shown that the protonated ligand is unidentate.[18]

The observation that the i.r. absorption of strong to medium intensity at *ca.* 1 600 cm^{-1} in the unprotonated complexes [Table 4(*a*)], which corresponds to the stretching of the unco-ordinated carbonyl group of the monothio-β-diketonate ligand, decreases in both intensity and frequency in the spectrum of the protonated analogues [Table 4(*b*)] is further confirmation that protonation has occurred to give the enolic structure (C).

A comparison of the symmetric and asymmetric vibrations ν(C–F) bands of the CF_3 group in $[M(CO)_5L^2]^-$ and $[M(CO)_5(HL^2)]$ with the free ligand (Table 7) shows that for the unprotonated complexes ν(C–F) decreases whereas the protonated derivatives show frequencies close to the free ligand. We would expect this behaviour if the proton were chelated by the ligand as in structure (C), and it is further evidence that in these complexes the ligands have structures analogous to the free ligands.

TABLE 7

Symmetric and asymmetric CF_3 vibrations (cm^{-1}) of L^2

Species	Symmetric	Asymmetric
HL^2 [a]	1 201	1 143
$[W(CO)_5L^2]^-$ [b]	1 189	1 135
$[W(CO)_5(HL^2)]$ [a]	1 200	1 155

[a] Neat. [b] Nujol mull.

[7/1465 *Received*, 11*th August*, 1977]

---

[18] M. C. Fredette and C. J. L. Lock, *Canad. J. Chem.*, 1973, **51**, 1116.