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Thiomorpholin-3-one Penta-carbonyl Derivatives with VIB Group Metals. Characterization and Structure

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Using thiomorpholin-3-one (tm) as ligand, the complexes [M(CO)$_5$tm] (where M = Cr, Mo, W) were prepared. They are crystalline yellow, diamagnetic and are non-electrolytes. The bonding of the ligand through the sulphur atom, suggested by i.r. data, was confirmed by the X-ray crystal structure analysis of [W(CO)$_5$tm], which showed that the compound has a slightly distorted octahedral symmetry. The crystals are monoclinic, space group P2$_1$/c with four molecules in a unit cell of dimensions a = 16.97(3), b = 6.43(2), c = 11.84(3) Å; β = 110.7(4)°. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by full matrix least squares methods to R = 0.070 for 1899 observed reflections.

Introduction

In order to investigate the competition between V and VI A donor atoms in the co-ordination to the metal atom, compounds of the general formula [M(CO)$_5$L] were prepared; the metals (M) were chromium(0), molybdenum(0) and tungsten(0) and the ligands

thiomorpholin-3-one
$\underline{\text{S–CH}_2\text{–CH}_2\text{–NH–CO–CH}_2}$ (*tm*)
thiomorpholin-3-thione
$\underline{\text{S–CH}_2\text{–CH}_2\text{–NH–CS–CH}_2}$ (*ts*)
thiazolidine-2-thione
S=$\underline{\text{C–S–CH}_2\text{–CH}_2\text{–NH}}$ (*ttz*)

Each of these ligands has three possible donor atoms, but because of steric hindrance it seems that they are not able to form chelates and act as monodentates, as previously demonstrated.[1–13]

The infrared analysis of [M(CO)$_5$ttz][10] and [M(CO)$_5$ts][12] showed that the =NH group is not involved in the co-ordination to the metal, and, on the basis of PMR data, it seems that the ligand is bonded *via* the thio-ketonic sulphur atom, the softest reaction center in the ligand molecules; a full confirmation of this hypothesis will be obtained by means of X-ray crystal structure analyses, now in progress.

In this paper the preparation and the characterization of M(CO)$_5$tm derivatives are reported.* They are yellow, crystalline, diamagnetic, air-stable compounds, soluble in common organic solvents and were obtained photometrically by uv-irradiation and TLC purification (see Table I).

TABLE I. Analytical Data and Some Physical Properties.[a]

Compound	Found			Required		
	M	C	H	M	C	H
[Cr(CO)$_5$tm]	16.98	34.22	2.95	16.82	34.96	2.28
[Mo(CO)$_5$tm]	–	30.62	2.11	–	30.61	2.00
[W(CO)$_5$tm]	–	24.65	1.33	–	24.51	1.60

[a] All compounds are yellow, air-stable, diamagnetic, non-electrolytes and soluble in common organic solvents.

Results and Discussion

The absorption spectra in the 2000 cm^{-1} region, taken in chloroform solution, are typical of penta-carbonyl species (a$_1$, b$_1$ and e modes are assigned). These vibrations fall at higher wave numbers than those of similar [M(CO)$_5$L] N-bonded compounds, suggesting the presence of S-bonded penta-carbonyl derivatives[14–16]; moreover the ν(NH) and ν(CO) absorptions do not significantly move when passing from the free ligand's to the complexes' spectra (see Table II).

Therefore, from the i.r. data the ligand seems to be bonded to the metal *via* the sulphur atom. The X-ray structure analysis of the tungsten derivative has completely confirmed this hypothesis. In fact, as shown in Figure 1, the co-ordination polyhedron around the

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* In a previous paper[6] the compounds [M(CO)$_4$tm$_2$] were described.

TABLE II. Assignments of the Most Important Infrared Absorptions in $CHCl_3$ Solutions (cm^{-1}).

		tm	$[Cr(CO)_5tm]$	$[Mo(CO)_5tm]$	$[W(CO)_5tm]$
ν(NH)		3407s	3402s	3404s	3400s[b]
ν(CO)[a]	$a_1(1)$	–	2078m	2080m	2080m
	b_1	–	1990w	1980w	1985w
	e	–	1945vs	1950vs	1940vs
ν(CO)		1660vs	1672vs	1670vs	1672vs

[a] The $a_1(2)$ mode is very little visible as a shoulder on the low frequency side of the e mode. [b] 3195 cm^{-1} in the solid state.

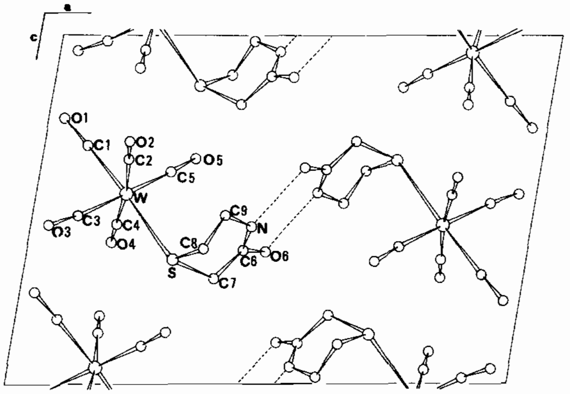

Figure 1. Projection of the structure along the b axis.

tungsten atom is a distorted octahedron formed by five carbon atoms of the carbonyl groups and the sulphur atom of the ligand molecule. Bond distances and angles are reported in Table III.

The W–C distances in the equatorial plane (*i.e.* the mean plane through C(2)–C(3)–C(4) and C(5) atoms) are in the range 2.01–2.08 Å, the highest difference with the average value (2.04 Å) being lower than 2σ. The pertinent C–O bond distances are very close.

The W–C(1) and W–O(1) (3.09 Å) bond distances are the lowest among the five, as a possible consequence of the *trans*-influence of the W–S bond; this effect has been recently reported for $(C_6H_5)_3PCr(CO)_5$ and $(C_6H_5O)_3PCr(CO)_5$.[17]

The W–C distances reported in the literature[18–21] generally fall around 1.95 Å, *i.e.* they are shorter then the values reported herein.

The W–S distance (2.55 Å) is in agreement with the value of 2.58 Å in $[W(\pi\text{-}C_5H_5)S_2W(CO)_4]$,[18] in which the metal is six-co-ordinated, and with those of 2.54 and 2.58 Å in the seven co-ordinated μ-chloro-(dichloromethyltin)-2,5-dithiohexanetricarbonyltungsten compound.[21] Our W–S distance is a little shorter than the sum of covalent radii values of sulphur and tungsten (1.04 and 1.58 Å, respectively).[22,21]

TABLE III. Bond Distances (Å) and Angles in $[W(CO)_5tm]$ with Estimated Standard Deviations (in parentheses).

Distances		Angles			
W–S	2.551(14)	C(1)–W–C(2)	88.1(6)	W–C(1)–O(1)	178.0(14)
W–C(1)	2.000(18)	C(1)–W–C(3)	88.4(6)	W–C(2)–O(2)	176.9(12)
W–C(2)	2.051(14)	C(1)–W–C(4)	85.7(6)	W–C(3)–O(3)	175.3(14)
W–C(3)	2.080(17)	C(1)–W–C(5)	89.1(7)	W–C(4)–O(4)	177.0(12)
W–C(4)	2.030(13)	C(2)–W–C(3)	89.1(6)	W–C(5)–O(5)	177.6(14)
W–C(5)	2.012(17)	C(2)–W–C(4)	173.2(5)	W–S–C(7)	111.4(6)
C(1)–O(1)	1.087(21)	C(2)–W–C(5)	92.6(6)	W–S–C(8)	113.7(6)
C(2)–O(2)	1.150(18)	C(3)–W–C(4)	88.0(6)	C(7)–S–C(8)	94.6(7)
C(3)–O(3)	1.133(21)	C(3)–W–C(5)	176.9(6)	S–C(7)–C(6)	115.5(11)
C(4)–O(4)	1.160(18)	C(4)–W–C(5)	90.1(6)	C(7)–C(6)–N	121.0(13)
C(5)–O(5)	1.148(21)	C(1)–W–S	175.6(4)	C(7)–C(6)–O(6)	119.2(14)
S–C(7)	1.807(16)	C(2)–W–S	93.6(4)	O(6)–C(6)–N	119.8(14)
S–C(8)	1.819(15)	C(3)–W–S	87.6(5)	C(6)–N–C(9)	128.2(12)
C(7)–C(6)	1.526(21)	C(4)–W–S	92.4(4)	N–C(9)–C(8)	112.2(12)
C(6)–N	1.329(21)	C(5)–W–S	94.8(5)	C(9)–C(8)–S	111.8(9)
C(6)–O(6)	1.233(20)				
C(9)–N	1.490(19)				
C(8)–C(9)	1.522(24)				

Assuming a tetrahedal distribution of the electron pairs in the sulphur atom, two different orientations are possible for the ligand molecule, one having the mean plane of the ring nearly perpendicular and the other nearly parallel to the mean equatorial plane as defined above. The latter orientation, which gives the most compact molecular configuration, is the one present in the crystal.

As seen in Table III, the S–W–C(3) angle is narrower while the S–W–C(2), –C(4) and –C(5) ones are wider than 90°, as a consequence of a van der Waals interaction between the ligand ring and the equatorial carbonyl groups. In fact the shorter contacts are: C(6)–C(5) 3.25; C(9)–C(2) 3.46; C(8)–C(2) 3.50; C(7)–C(5) 3.55; C(9)–C(5) 3.56 Å.

As far as the ligand ring is concerned, all the distances are typical of single bond values, except C(6)–N; this is the consequence of the resonance effect in the N–C–O system, whose bond distances are very close to those found in the urea molecule.[23]

Taking the cyclohexane molecule as a reference, we observe that the C(8)–S–C(7) angle is narrower and that the C–S bond distances are longer. These facts explain the remarkable puckering in the *tm* molecule (the dihedral angle between the mean plane through the C(6,7,8,9) atoms and the C(7)–C(8)–S plane is 130.4°. *Viceversa,* on the opposite side of the ring, the C–N–C angle is wider and the N–C distances are shorter and, therefore, the puckering is less marked (the pertinent dihedral angle is 162.8°).

Molecular packing shows short O····N contacts (2.88 Å), practically equal to the van der Waals radii sum (2.90 Å) between molecules around the centre of symmetry at $^1/_2 0 0$ and $^1/_2 0 ^1/_2$. These contacts should be interpreted as inter-molecular hydrogen bonds because the calculated position of the hydrogen atom falls near the O···N axis. This fact is in agreement with ν(NH), which exhibits a negative shift (from 3400 to 3195 cm^{-1}) on going from the dilute solution to the solid state spectra.

Experimental

Preparation of the Compounds

An equimolecular THF solution of [M(CO)$_6$] (where M = Cr, Mo and W) with the ligand was irradiated with an uv Osram source for about 30 min under nitrogen. The yellow solution was evaporated under reduced pressure and the solid residue was extracted in Soxlet with petroleum ether to eliminate the unreacted [M(CO)$_6$]. After water wash, the crude product was purified by TLC (silica gel, Merck HF$_{254}$) eluting with benzene. The single crystal of [W(CO)$_5$ tm] was obtained by slow crystallization from a CH$_2$Cl$_2$/ligroine mixture.

Spectrophotometric Measurements

The i.r. spectra were recorded in the range 4000–260 cm^{-1} using a Perkin–Elmer model 325 spectrophotometer as KBr discs or in CHCl$_3$ solutions. The most important absorptions in solid state are (cm^{-1}): [Cr(CO)$_5$tm] 3300m, 3195m, 3080m, 3050m, 3000w, 2960w, 2920m (for carbonyl stretchings see Table II), 1655vs, 1495s, 1465m, 1420m, 1385s, 1345s, 1290m, 1240m, 1218m, 1194m, 1158s, 1125m, 1015s, 965m, 928s, 868s, 840m, 815m, 770s, 668s, 640vs, 548m, 473s, 450s, 430m, 418w, 405m, 385m, 365m. [Mo(CO)$_5$tm] 3300m, 3195s, 3150sh, 3110sh, 3080m, 3050m, 3000w, 2960w, 2920m (for carbonyl stretchings see Table II), 1655vs, 1495s, 1462s, 1420m, 1385s, 1345vs, 1289m, 1245m, 1219m, 1195m, 1158s, 1128s, 1058w, 1015s, 995vw, 965s, 928s, 868s, 845m, 818m, 770s, 675m, 670vw, 648s, 610vs, 580vs, 530m, 470s, 442w, 428s, 404s, 375vs, 364vw, 355vs, 305w. [W(CO)$_5$tm] 3300m, 3195s, 3150sh, 3110sh, 3080m, 3040m, 3000w, 2960w, 2920m (for carbonyl stretchings see Table II), 1652vs, 1495s, 1462s, 1440vw, 1420m, 1385vs, 1345vs, 1288m, 1245m, 1228m, 1194s, 1158s, 1125m, 1060w, 1015s, 1000vw, 965s, 928s, 904w, 870s, 840m, 815m; 770s, 672s, 648s, 600vs, 572vs, 540vw, 472s, 455w, 425s, 400vw, 300vs, 370vs, 360vs, 310w.

The uv spectra were recorded in CHCl$_3$ solutions with a Perkin–Elmer model 402. Maxima wave numbers (cm^{-1}), ε values in parentheses: [Cr(CO)$_5$tm] 25300 (1800); [Mo(CO)$_5$tm] 34500 (5800); 26600sh (~560); [W(CO)$_5$tm] 34200 (4300), 26700 (2100).

Other Measurements

Conductivity measurements, carried out in MeOH solutions with a WTW bridge at 20° C, demonstrated that all compounds are non-electrolytes. Magnetic measurements carried out at room temperature by the Gouy method with a Newport instrument, showed that all compounds are diamagnetic.

Crystal Data

Monoclinic space group P2$_1$/c; a = 16.97(3), b = 6.43(2), c = 11.84(3) Å; β = 110.7(4)°; U = 1209 Å^3; m.w. = 440.92; D$_m$ = 2.40, D$_c$ (Z = 4) = 2.42 g cm^{-3}; F (000) = 796; μ = 109.6 cm^{-1}; λ(MoK$_\alpha$) = 0.7107 Å. Unit cell parameters and their estimated standard deviations were determined by a least-squares fit for 17 values of Θ, χ, Φ accurately measured by use of a very narrow counter aperture.

Intensity Measurements

A crystal of dimensions 0.60 × 0.20 × 0.13 mm was mounted on the Siemens automatic single-crystal diffractometer AED, with the b axis nearly coincident with the polar Φ-axis of the goniostat. The procedure was similar to that previously described.[24] The ω-scan technique with a "five value" measuring procedure

TABLE IV. Atomic Coordinates (× 10^4) and Anisotropic[a] Temperature Factors, with Standard Deviations in Parentheses.

	X/a	Y/b	Z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	1791(0)	678(1)	4559(0)	21(0)	125(2)	31(1)	–1(0)	13(0)	–3(0)
S	2914(2)	2149(5)	6447(3)	24(1)	159(8)	39(3)	–5(2)	17(1)	–18(4)
O1	342(9)	–1146(23)	2396(13)	50(7)	293(33)	80(13)	–41(13)	14(8)	–28(19)
O2	1675(8)	4844(21)	3027(10)	51(6)	202(31)	67(10)	–1(12)	28(6)	6(16)
O3	366(8)	2537(20)	5477(12)	50(6)	252(31)	125(14)	18(10)	64(8)	–12(16)
O4	1654(7)	–3480(21)	5946(11)	40(5)	267(35)	94(12)	–15(11)	37(6)	25(17)
O5	3069(8)	–1505(21)	3539(11)	49(6)	279(35)	73(10)	12(12)	41(6)	–10(16)
O6	4749(7)	–1326(19)	6209(9)	48(5)	188(26)	44(8)	36(10)	22(5)	14(13)
N	4391(7)	1852(18)	5481(10)	29(5)	206(33)	48(10)	30(10)	21(5)	48(15)
C1	850(9)	–469(21)	3148(13)	24(6)	183(37)	35(11)	5(10)	12(7)	24(16)
C2	1735(8)	3327(20)	3567(12)	30(5)	116(32)	54(12)	–1(10)	23(6)	11(16)
C3	892(10)	1950(23)	5180(15)	38(6)	157(37)	90(15)	27(12)	29(8)	15(18)
C4	1703(8)	–2000(19)	5414(12)	25(5)	106(30)	41(11)	13(9)	15(6)	28(14)
C5	2619(11)	–683(19)	3925(15)	37(8)	147(38)	56(14)	–12(11)	25(9)	–8(15)
C6	4343(8)	277(27)	6182(15)	9(4)	229(41)	74(15)	7(11)	14(7)	–9(21)
C7	3817(9)	446(22)	6991(13)	16(5)	191(38)	45(12)	15(9)	3(6)	25(16)
C8	3499(11)	4315(17)	6144(16)	33(7)	109(32)	70(15)	–20(9)	24(8)	–56(15)
C9	3868(9)	3775(23)	5180(15)	27(6)	127(29)	85(15)	9(11)	28(7)	0(19)

[a] In the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

was used. A total of 2022 independent intensities up to $2\Theta \leqq 50°$ were recorded. The intensities of three standard reflections were measured after every 200 reflections and their net counts did not vary noticeably during data collection (*ca.* 5 days). The standard deviations were calculated as $\sigma^2(I) = P + B$, where P is total integrated peak count, B is the total background count. The intensities were corrected for the Lorentz-polarization effect. No absorption or extinction corrections were applied. 123 reflections with $I/\sigma(I) < 2$ were not used in the analysis.

Solution and Refinement of the Structure

The positions of the tungsten, sulphur and two light atoms were determined by a three-dimensional Patterson synthesis; two successive F_o and $(F_o–F_c)$ three-dimensional Fourier syntheses gave the positions of the remaining non hydrogen atoms. The R-factor (where $R = \Sigma [||F_o|-|F_c||/\Sigma|F_o|]$, using the overall temperature and the scale factors derived from a Wilson plot, was 0.25 for 1899 observed reflections. Both positional and isotropic thermal parameters were then refined by the block-diagonal least-squares method using the program written by R. Shiono for the IBM 1130 computer; the minimized quantity was $\Sigma w(F_o–F_c)^2$, where $w = 4F_o^2/[\sigma^2(F_o^2) + (0.12\ F_o^2)^2]$.[25] Five cycles reduced the R factor to 0.090.

At this stage the hydrogen atoms were introduced at calculated positions and given an isotropic B value of 4.5 Å, but their parameters were held fixed in the next cycles. Two more cycles, using the ORFLS program as adapted to the IBM 360/67 of CNUCE, Pisa,[26] and anisotropic thermal parameters reduced R and R_w values (where $R_w = \Sigma w(F_o–F_c)^2/\Sigma wF_o^2$) to 0.070 and 0.110 respectively for 1899 refined reflections. The values of the goodness of fit S was 1.8 (where $S = [\Sigma w(F_o–F_c)^2/(m–n)]^{1/2}$; *m* is the number of observations and *n* the number of variables). The final R value for the 2022 measured reflections is 0.072.

The atomic scattering factors were interpolated from the values given in "International Tables for X-ray Crystallography".[27] The final atomic parameters with estimated standard deviations are given in Table IV. Observed and calculated structure factors are available on request from the Authors.

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