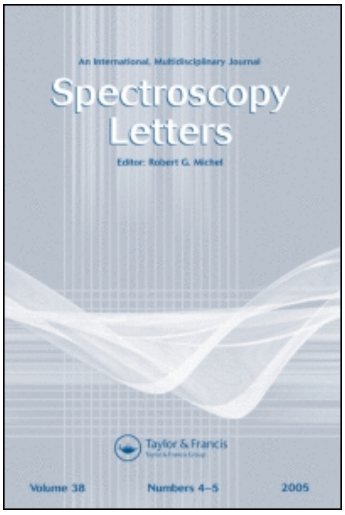

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Hickey, James P. , Baibich, Ione M. , Butler, Ian S. and Todd, Lee J.(1978) 'Oxygen-17 NMR Spectra of Some Group VIB and VIIB Transition Metal Chalcarbonyl Complexes', Spectroscopy Letters, 11: 9, 671 — 680
To link to this Article: DOI: 10.1080/00387017808063439
URL: http://dx.doi.org/10.1080/00387017808063439

SPECTROSCOPY LETTERS, 11(9), 671-680 (1978)

OXYGEN-17 NMR SPECTRA OF SOME GROUP VIB AND VIIB TRANSITION METAL CHALCOCARBONYL COMPLEXES

Key words: oxygen-17 nmr, transition metals , metal carbonyls, metal thiocarbonyls, metal selenocarbonyls, metal chalcocarbonyls, chromium, molybdenum, tungsten, manganese

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INTRODUCTION

Although there are numerous reports in the literature on the ^{13}C nmr spectra of transition metal carbonyls,[1] little attention has thus far been focused on their ^{17}O nmr spectra.[2-4] Oxygen-17 nmr spectra are extremely difficult to obtain because of the quadrupolar nature of the ^{17}O nucleus (I = 5/2) and its low natural abundance (0.037%). In addition, the low

solubility of many metal carbonyl complexes makes ^{17}O nmr spectroscopy for these systems even more difficult. Nevertheless, some spectra have been obtained and we have already made a detailed comparison of the ^{17}O and ^{13}C nmr spectra of several chromium chalcocarbonyl complexes of the general formula, $(\eta^6\text{-Arene})Cr(CO)_2(CX)$ (X = O, S).[3] In this present communication, we report the ^{17}O nmr spectra of some representative examples of Group VIB and VIIB transition metal chalcocarbonyl complexes and discuss the some of the electronic effects which cause variations in the ^{17}O shielding values.

RESULTS AND DISCUSSION

The $\delta(C^{17}O)$ chemical shifts for the various complexes are given in Table 1 together with the associated $\delta(^{13}CO)$ values. In most cases, the ^{13}C nmr data have been reported previously[1a,3,4] but they were remeasured in the present study for the sake of internal consistency. For both ^{17}O and ^{13}C, there was no evidence of coupling to the metal nuclei. The ^{17}O shielding values fall within the 300-400 ppm range (downfield from $^{17}OH_2$) found previously for several other metal carbonyl derivatives.[2-4]

A "metal triad" effect[1a] is observed for $\delta(C^{17}O)$ chemical shifts of the Group VIB metal complexes, $M(CO)_6$ (M = Cr, Mo, W),[4] $M(CO)_5(CS)$ (M = Cr, W)[5] and $(\eta^6\text{-}C_6H_5CH_3)M(CO)_3$ (M = Cr, W).

On descending the group, the ^{17}O shielding values shift about 10 ppm upfield per change in metal. A similar effect, but in the opposite sense, has been noted for the ^{13}C nmr spectra of the metal hexacarbonyls.[1a] The origin of these effects are not yet clear but it has been suggested that the diamagnetic shielding influences of the metal nuclei play an important role. In the case of ^{13}C shieldings, Braterman[7] has proposed that paramagnetic currents, dependent on d-d transitions of the metal, may also make a contribution to the ^{13}C chemical shift.

For the Group VIB $M(CO)_5(CX)$ complexes, where both cis and trans carbonyl oxygen ^{17}O resonances were observed, the ^{17}O nmr spectra show the trans resonance downfield of the cis resonance, while the corresponding ^{13}C nmr spectra show the opposite trend. For $Cr(CO)_5CS$, both cis and trans ^{13}C resonances are observed while only a single ^{17}O nmr resonance (proposed cis based on the $Cr(CO)_5CSe$ ^{17}O spectrum) is observed. This single ^{17}O nmr resonance may be the result of either accidental degeneracy of the cis and trans resonances or extreme broadening of the trans resonance due to a very large correlation time.[4] Decomposition in solution at higher temperatures prevented a high temperature ^{17}O nmr investigation for the purpose of decreasing the correlation time,[8] which would narrow the line

TABLE 1

^{17}O and ^{13}C NMR Spectra (ppm) of Some Representative Transition Metal Chalcocarbonyl Complexes

Complex	$\delta(C^{17}O)$, ppm[a]		$\delta(^{13}CO)$, ppm[b]		$\delta(^{13}CX)$, ppm[c]
	cis	trans	cis	trans	
$(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$	372.8		225.4[c]		-
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	374.3		224.5[c]		-
$(\eta^5\text{-}C_5H_5)Mn(CO)_2CS$	376.8		224.0[c]		335.4
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$[d]	370.7		233.4		-
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CS)$[d]	374.1		231.5		346.4
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe)$	375.7		229.0		363.7
$(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$[d]	370.0		233.7		-
$(\eta^6\text{-}C_6H_5CH_3)W(CO)_3$[e,f]	345.9		210.1		-
$Cr(CO)_6$[g]	376.2		212.2		-
$Cr(CO)_5(CS)$	373.0	(h)	212.4 (i)	209.4	332.2
$Cr(CO)_5(CSe)$	373.4	385.3	211.7	208.1	360.7
$Mo(CO)_6$[g]	364.9		202.0		-
$W(CO)_6$[g]	355.5		192.1		-
$W(CO)_5(CS)$	357.0	364.4	192.4 (i)	189.3	298.7

[a] Measured to ±0.15 ppm in dry, degassed, saturated CH_2Cl_2 solutions on a Varian XL-100-15 FTNMR spectrometer at 13.57 MHz. Values quoted are relative to an external sample of ^{17}O-enriched H_2O as reference where $\delta(^{17}OH_2) = 0.00$ ppm.

[b] Except where otherwise noted, samples were measured to ±0.1 ppm on a Bruker WH90 FTNMR spectrometer at 22.63 MHz. Values quoted are relative to TMS using $(D_3C)_2CO$ or $C_6D_5CD_3$ as lock where δ(TMS) = 0.00 ppm. 0.1M $Cr(acac)_3$ was added to each solution to aid in carbonyl T_1 relaxation.

continued

width and increase the resolution of the trans resonance.

In the case of the $M(CO)_5(CX)$ series, (M=Cr, X=O,S,Se ; M=W, X=O,S), the ^{17}O and ^{13}C nmr chemical shifts for the cis resonances are relatively insensitive to the change from C(O) to C(S,Se); the ^{17}O shielding values are shifted approximately 3 ppm upfield from the parent hexacarbonyl ^{17}O resonances, while the corresponding ^{13}C resonances show a 1-2 ppm shift downfield. The trans ^{17}O and ^{13}C resonances (where observed) are more affected by the change in chalcogen. The ^{17}O resonances exhibit a 9 ppm downfield shift in $Cr(CO)_5CSe$ and $W(CO)_5CS$; the ^{13}C chemical shifts appear approximately 7 ppm and 3 ppm upfield, respectively. Substitution by other Lewis bases (e.q., tertiary phosphines) causes the opposite pattern in

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footnotes to Table I continued

[c] Ref. 9

[d] Ref. 3

[e] ^{13}C nmr spectra measured to ±0.1 ppm in dry, degassed saturated CH_2Cl_2 solutions on a Varian XL-100-15 FTNMR at 25.20 MHz. Values quoted are relative to TMS using the CH_2Cl_2 solvent peak as internal reference where $\delta(TMS) = \delta(CH_2Cl_2) + 53.89$ ppm. To aid in carbonyl T_1 relaxation, 0.05M $Cr(acac)_3$ was added to each sample.

[f] $\delta(^{13}C)$(ligand ring resonances): 109.9(C_1); 92.8, 90.7($C_{2,5}$,$C_{3,4}$); 87.8(C_4); 20.5(CH_3) ppm. No coupling ($J_{^{183}W-^{13}C}$) was observed to either CO or the arene ring.

[g] Ref. 4

[h] Not observed.

[i] Only the cis value was actually reported previously; see Ref. 5.

both the ^{17}O nmr[4] and ^{13}C nmr[1] spectra. The cis resonances are only slightly affected, being shifted downfield in the ^{17}O nmr and upfield in the ^{13}C nmr. The trans resonances are again more affected, the ^{17}O resonance being shifted upfield and the ^{13}C resonance downfield. The well-documented "trans effect" for octahedral transition metal complexes appears to apply to all three chalcocarbonyl ligands and affects the ^{17}O nmr chemical shift as well as the ^{13}C chemical shift.[1]

For the $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X=O,S,Se) series, the ^{17}O chemical shift shows a progressive upfield shift on going down the chalcogen family, while the ^{13}C spectra show the opposite trend. In both the ^{17}O and ^{13}C spectra, the shifts from O to S are larger than that for S to Se. The explanation for this is unclear at present.

For the manganese series, $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CX)$ (X = O, S), going down the chalcogen family shows that $\delta(C^{17}O)$ shifts downfield while the corresponding $\delta(^{13}CO)$ values shift upfield. This behavior was also observed for the respective ^{17}O and ^{13}C carbonyl oxygen and carbon chemical shifts in the series $(C_6H_{6-n}R_n)Cr(CO)_2$-(CX) (X=O,S)[3]. Unlike the manganese carbonyl ^{13}C resonances,[9,10] no room temperature broadening of the respective carbonyl ^{17}O resonance is observed.[10]

This is presumably due[6] to a weakened transmission of quadrupolar and spin-coupling effects of the manganese nucleus [^{55}Mn,I=5/2 (100%)] on to the oxygen atom through two bonds, while the carbon atom is only one bond away.[4] For those substituted metal carbonyl complexes which have now been studied by both ^{13}C and ^{17}O nmr the carbonyl carbon ^{13}C chemical shifts appear at lower fields than for those of the parent carbonyl complexes,[1] while the converse is true for the ^{17}O chemical shifts.[3,4] In the present work, however, substitution of one CO ligand by CS or CSe causes the carbonyl oxygen ^{17}O resonance(s) of the remaining CO groups to shift downfield, while the corresponding ^{13}C chemical shift(s) move upfield relative to those for the parent complex.

Molecular orbital calculations for the CS moiety[11] and photoelectron spectroscopic studies on $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ and $Cr(CO)_5(CS)$[12] show CS to be both a better σ-donor and π-acceptor ligand than CO, and this can be extended to CSe. Also, X-ray crystallographic[13,14] and mass spectroscopic evidence[15,16] show that metal-C(S) bonds are much stronger than metal-C(O) bonds. Mass spectrometric studies on $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$, $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(CSe)$ and $(\eta^5\text{-}C_5H_5)Re(CO)_2(CSe)$ indicate that this is also for the metal-C(Se) bond.[17] The observed chemical behavior of thio- and selenocarbonyl

complexes on nucleophilic substitution supports these contentions.[15,17,18]

It is thus reasonable to conclude that both the downfield chemical shifts of the carbonyl ^{17}O resonances in the $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$, $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X=S,Se), and $M(CO)_5CX$ (X=Cr, X=S,Se; M=W, X=S) complexes and the ^{17}O chemical shift patterns are a result of the greater net electron attracting (σ-donor vs. π-acceptor) ability of the CS and CSe ligands as compared to CO. A similar conclusion was reached from a ^{13}C nmr study on a series of Group VIIB $(\eta^5\text{-}C_5H_4R)M(CO)_2(CX)$ (M=Mn,Re; X=O,S,Se) complexes.[9]

A further conclusion is that the opposing trends for respective carbonyl ^{17}O and ^{13}C resonances observed to date [2-4] result from the synergistic bonding associated with transition metal-CO linkages.

ACKNOWLEDGEMENTS

We thank the National Research Council of Canada and the National Science Foundation (USA) for support in this work. Dr. Art Clouse (Indiana U.) and Dr. Gordon Hamer (McGill U.) are thanked for their advice and help with the operation of the two NMR spectrometers. One of us (I.M.B.) thanks CAPES (Brazil) for the award of a graduate fellowship.

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Received 6- 2-78
Accepted 6-28-78