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Preliminary communication

STRUCTURE OF trans-$W(CO)_4(CNC_6H_{11})(CS)$ AND A CORRELATION OF ν(CS) FREQUENCIES WITH C-S BOND DISTANCES IN METAL THIOCARBONYL COMPLEXES*

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SUMMARY

An X-ray structural investigation of trans-$W(CO)_4(CNC_6H_{11})(CS)$ shows that the W-C bond distances to the 3 isoelectronic ligands increase in the order: W-CS(1.944Å) < W-CO(2.0645Å, average) < W-CNC_6H_{11}(2.158Å). Using data from this molecule as well as results from other thiocarbonyl complexes reported in the literature, an excellent correlation of low ν(CS) frequencies with long C-S bond distances is observed, a trend which supports current bonding theories for thiocarbonyl complexes.

The X-ray structural investigation of trans-$W(CO)_4(CNC_6H_{11})(CS)$ was undertaken in order to allow a direct comparison of W-C bond distances to carbon monosulfide, carbon monoxide and cyclohexylisocyanide ligands. In addition, it has provided results which allow the correlation of

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ν(CS) frequencies with C-S bond distances previously reported in the literature.

The complex was prepared by the reaction of *trans*-W(CO)$_4$(I)(CS)$^-$ with Ag$^+$ in acetone solution followed by the addition of cyclohexylisocyanide [1]. Crystals were grown from pentane solution at -20°C, and a single crystal was selected for X-ray diffraction study. Use of an automatic indexing routine coupled with analysis of oscillation photographs indicated a monoclinic crystal system, and the space group $P2_1/n$ was uniquely specified by the extinction conditions. The unit ce parameters are $a = 11.645(3)$, $b = 21.205(6)$, and $c = 6.146(3)$Å, $\beta = 92.10(5$ Intensity data were collected on a computer-controlled four circle diffractometer equipped with a scintillation counter utilizing graphite-monochromated Mo $K\alpha$ radiation. Data were corrected for absorption, and positions of all non-hydrogen atoms were determined by a combination of Patterson analysis and electron density map calculations. Figure 1 show a computer drawing (excluding hydrogens) of the molecular structure resulting from refinement to a conventional crystallographic discrepanc factor of $R = 6.5\%$ based on 1862 intensities with $I > 3\sigma(I)$.

Of the W-C bond distances (in Å), the W-CS value of 1.944(19) is the shortest. The W-CO distances are longer: W-C$_1$, 2.066(23); W-C$_2$, 2.056(22); W-C$_3$, 2.089(28); W-C$_4$, 2.047(22). The W-CNC$_6$H$_{11}$ distance is the longest at 2.158(23). This trend supports other arguments [2] which indicate that metal-to-ligand π back-bonding decreases in the order: W-CS > W-CO > W-CNC$_6$H$_{11}$.

The C-S distance is 1.564(19), and the W-C$_5$-S angle is essentially linear, 179.0(1.2)°. The C$_6$-N and N-C$_7$ distances are 1.160(24) and 1.535(27), respectively, and the W-C$_6$-N and C$_6$-N-C$_7$ angles are 175.5(2. and 173.4(2.2)°, respectively. The C-O bond distances range from 1.104 to 1.155(26), and the W-C-O angles range from 176.2 to 179.3(1.9)

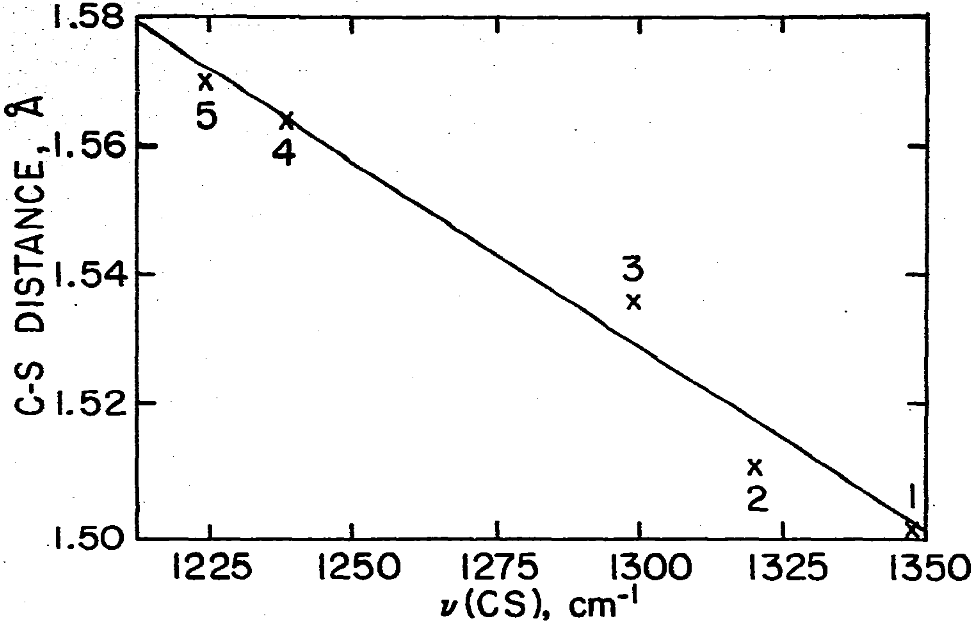

Figure 1. Molecular configuration of *trans*-$W(CO)_4(CNC_6H_{11})(CS)$.

The geometry around the W is octahedral with all C-W-C angles being 90.0 ± 2.8°.

The bonding of CO, CNR, and CS to transition metals is postulated to involve π back-bonding from the metal $d\pi$ orbitals to the π^* orbitals on the ligands. Such back-bonding should weaken the C-X bond resulting in decreased C-X stretching frequencies, as well as increased C-X bond lengths. Because of the very small changes [3] observed in C-O bond distances in metal carbonyl complexes with different electronic environments, it has not been possible to confirm these theoretical predictions using C-O bond length data. Fortunately, this confirmatory evidence is now available for thiocarbonyl complexes.

X-Ray structural determinations for 5 complexes containing terminal thiocarbonyl ligands are now available (Table 1). As for CO, π-bonding arguments for thiocarbonyl complexes suggest that complexes with low ν(CS) frequencies should have long C-S bond distances. In Figure 2 is shown a plot of ν(CS) versus C-S bond distances for these complexe While the errors in C-S distance are reasonably large in complexes wit the heavier metals, the correlation is unmistakeable. Those complexe with the least available metal π-orbital electron density (such as the cationic complexes 1 and 2) have the shortest C-S distances, while mo electron-rich metal complexes have longer C-S distances.

Although not indicated in Figure 2, even ν(CS) and C-S distance data (Table 1), for free gaseous CS fall close to the least squares li shown in the Figure. The data in Table 1 show that there are complexe in which ν(CS) is higher and the C-S distance is shorter than in free CS itself. This observation supports molecular orbital arguments [2b, 15] which indicate that the σ-donor electrons of CS are antibondi

TABLE 1. C-S BOND DISTANCES AND ν(CS) FREQUENCIES

No.	Compound	ν(C-S), cm^{-1}	C-S, Å
1	$[(\eta\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$	1348^a	$1.501(4)^b$
2	$[Ir(PPh_3)_2(CO)_2(CS)]PF_6$	1321^c	1.512(26), 1.509(24
3	trans-$RhCl(PPh_3)_2(CS)$	1299^e	$1.536(10)^f$
4	trans-$W(CO)_4(CNC_6H_{11})(CS)$	$1240^{g,h}$	$1.564(19)^h$
5	$(\eta\text{-}C_6H_5CO_2CH_3)Cr(CO)_2(CS)$	1225^i	$1.570(2)^j$
	CS	1274^k	$1.5349(2)^l$
	cis-$[(\eta\text{-}C_5H_5)Fe(CO)(CS)]_2$	$1124^{m,n}$	1.592(8), 1.587(7)

[a] Nujol, ref. 4. [b] Ref. 5. [c] $CHCl_3$, ref. 6. [d] Ref. 7. [e] C_6H_6, ref. 8. [f] Ref. 9. [g] CS_2. [h] This work. [i] CCl_4, ref. 10. [j] Ref. 11. [k] Ref. 12. [l] Ref. 13. [m] CS_2. [n] Ref. 14.

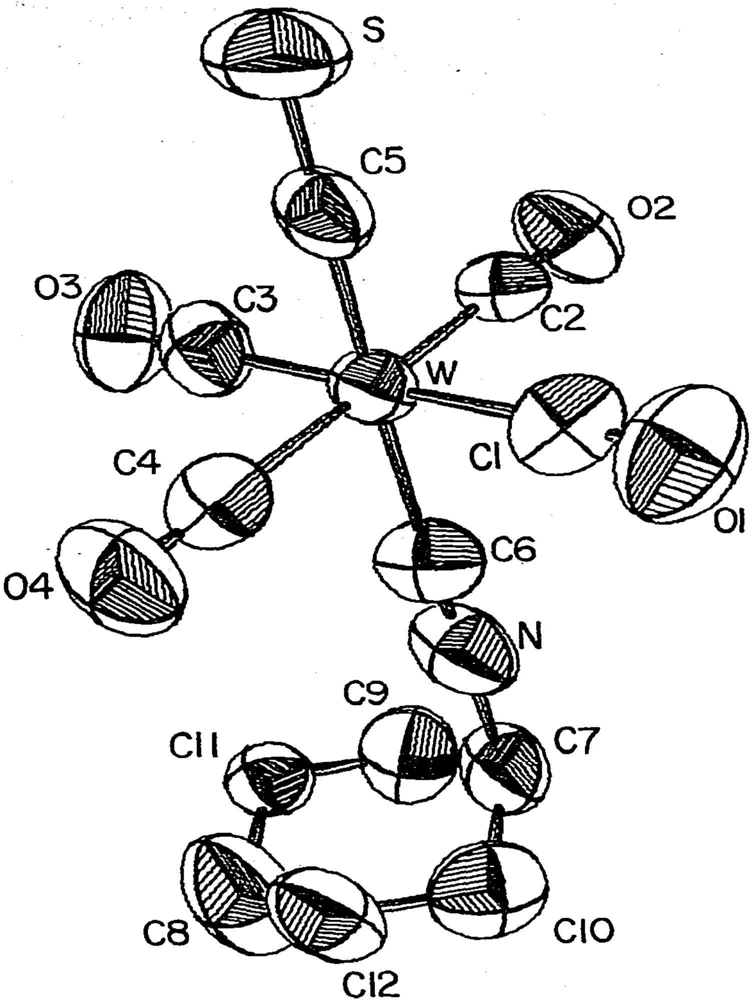

Figure 2. Correlation of ν(CS) frequencies and C-S bond distances for the compounds numbered in Table 1.

with respect to the CS bond. Thus, in complexes where there is reduced π-bonding, σ-donor effects will predominate and strengthen the C-S bond.

While data [14] for the bridging CS groups in cis-[(η-C_5H_5)Fe(CO)-(CS)]$_2$ are included in Table 1, they do not fall on a linear extrapolation of the line in Figure 2. Nevertheless, the correlation provides a useful method of obtaining C-S bond distances from ν(CS) frequencies for complexes with terminal thiocarbonyl ligands.

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