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(19) Two cyclic peptides which were not expected to bind amino acid salts *specifically* were studied under similar conditions. In *cyclo*$(Pro)_3$, the three rigid Pro C═O groups are oriented away from the center of the peptide in a manner unfavorable for cooperative cation binding.[20] Valinomycin, a naturally occurring cyclic depsipeptide, has a binding site in the interior of the molecule which would not be accessible to bulky amino acid cations.[21,22] Upon addition of D,L-Phe-OMe · HCl up to a twofold molar excess in chloroform solutions, no chemical shift changes in spectra of either of the cyclic peptides (or in the salt) were noted, suggesting that the observed changes in spectra of *cyclo*$(Pro\text{-}Gly)_n$ peptides and added salts result from specific, cooperative binding. Note that nonspecific binding of an alkylammonium group to an individual peptide carbonyl group, which may occur in chloroform, was also not manifested by any ^{13}C chemical shift changes.

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Charles M. Deber, Elkan R. Blout*
Department of Biological Chemistry, Harvard University Medical School
Boston, Massachusetts 02115

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End-to-End Bridging by the Thiocarbonyl Ligand. Complexes of the Type MC≡SM′

Sir:

Only a small number of oxygen-bonded adducts of terminal metal carbonyl derivatives have been isolated,[1] and there is spectroscopic evidence for only a few additional such adducts.[2] It is apparent from these few examples that a high electron density on the carbonyl ligand, indicated by a low carbonyl stretching frequency, is a prerequisite for adduct formation. In all cases the adducted carbonyl exhibits a lowered CO stretching frequency, while any other carbonyl groups in the complex have absorptions shifted to higher frequency.

Based on a comparison of organic carbonyl and thiocarbonyl compounds,[3] the thiocarbonyl ligand may be expected to be more polar and reactive than analogous carbonyl ligands. Evidence supporting this idea derives from the observed ease with which thiocarbonyls undergo nucleophilic attack at the carbon,[4] as in eq 1. However, until now there

$$(CO)_5WC\equiv S + RNH_2 \longrightarrow (CO)_5WC\equiv NR + H_2S \quad (1)$$

has been no chemical evidence for high electron density on the sulfur. In view of the larger anticipated negative charge on the sulfur atom and its lower electronegativity as compared to oxygen, Lewis acids may form sulfur-bonded adducts of suitable metal thiocarbonyls even under circumstances where the carbonyl ligand does not. We now report the first examples of such complexes.

We observed that $W(CO)_5(CS)$[4] and *trans*-$W(CO)_4(PPh_3)(CS)$,[4] having relatively high CS stretching frequencies (Table I), do not react with mercuric halides or BCl_3 at 25° in CH_2Cl_2 solvent. The complex *mer*-$W(CO)_3(CS)(DPE)$ (DPE = ethylenebis(diphenylphosphine)), prepared by refluxing equimolar amounts of $W(CO)_5(CS)$ and DPE in xylene for 2 hr, has a lower CS absorption but also does not react with these reagents. However, $W(CO)(CS)(DPE)_2$ (**1**), having the lowest CS stretching frequency (1161 cm^{-1}) yet reported for a metal thiocarbonyl ligand, does react with a variety of Lewis acids. This complex was prepared in good yield (>80%) by heating equimolar $W(CO)_3(CS)(DPE)$ and molten DPE under N_2 at 195° for 1 hr. The crude product could be recrystallized from CH_2Cl_2 or CS_2. The carbonyl and thiocarbonyl groups are presumed to be cis in this complex, based on the geometry of its precursor, *mer*-$W(CO)_3(CS)(DPE)$.

Table I. Infrared Data

Compound	$\nu(CO)$,[a] cm^{-1}	$\nu(CS)$,[a] cm^{-1}
$W(CO)_5(CS)$	2096 (w), 2007 (m), 1989 (vs)[b]	1258 (vs)[b]
trans-$W(CO)_4(PPh_3)(CS)$	2052 (w), 1981 (vw), 1956 (vs)[b]	1247 (vs)[b]
mer-$W(CO)_3(CS)(DPE)$	2013 (w), 1925 (vs)	1215[c]
$W(CO)(CS)(DPE)_2$	1838 (s)	1161 (s)
$W(CO)(DPE)_2CSW(CO)_5$	2062 (w), 1925 (vs), 1878 (m)	*d*
$W(CO)(DPE)_2CSHgCl_2$	1885	*d*
$W(CO)(DPE)_2CSHgI_2$	1872	*d*
$\{[W(CO)(DPE)_2CS]_2Ag\}BF_4$	1869 (s)[e]	1106 (s)[e]

[a] Recorded in CH_2Cl_2 unless specified otherwise. [b] *n*-Hexane solution. [c] CS_2 solution. [d] Absorption is partially obscured by a ligand absorption and an exact value could not be obtained. [e] Nujol mull.

When stirred in CH_2Cl_2 with an equimolar amount of the reactive $W(CO)_5(acetone)$,[5] **1** forms an orange complex (>80% yield), which was recrystallized from CH_2Cl_2–hexane or CS_2. Elemental analyses indicate a composition of

$$W(CO)(CS)(DPE)_2 + (Me_2CO)W(CO)_5 \longrightarrow (DPE)_2(CO)WC\equiv SW(CO)_5 + Me_2CO \quad (2)$$

$(DPE)_2(CO)W(CS)W(CO)_5$ for this compound (Calcd: C, 51.45; H, 2.87; S, 2.32. Found: C, 51.76; H, 3.54; S, 1.75). The complex shows evidence of some decomposition in acetone solution in minutes but is stable in the solid state for several days. This is the first complex known to contain a bridging thiocarbonyl ligand; its end-to-end bridging (*via* C and S) structure contrasts with the carbon-bridging form (*via* only the carbon) observed for CO bridging of transition metals. The infrared spectrum (Table I) of the product shows the three expected carbonyl absorptions of the $W(CO)_5$ moiety, and the lowest of these apparently overlaps the lone carbonyl absorption of the $W(CO)(CS)(DPE)_2$ fragment. This carbonyl band has therefore shifted to higher frequency as compared to its position in the starting complex, **1**. The thiocarbonyl absorption, however, has not shifted to higher frequency since no new bands appear in the ir spectrum from 1160 to 1400 cm^{-1}, and the CS band originally near 1160 cm^{-1} has disappeared. It is apparently overlapped by a strong, broad DPE ligand absorption near 1095 cm^{-1} since this absorption has become more intense.

This novel binuclear complex, bridged only by the CS ligand, reacts with PPh_3 in CH_2Cl_2 solution at 25° to yield, within several minutes, **1** and $W(CO)_5PPh_3$.[7] It was hoped that W–C cleavage might occur in this reaction to give the isothiocarbonyl complex $(C\equiv S)W(CO)_5$; this was not observed, however.

The reaction of **1** with an equimolar amount of $HgCl_2$ or HgI_2 in CH_2Cl_2 (eq 3) gives orange[8] or red crystals,[9] respectively (>80% yield), when hexane is added to the solu-

$$\mathrm{W(CO)(CS)(DPE)_2 + HgX_2 \longrightarrow (DPE)_2(CO)WC{\equiv}SHgX_2} \qquad (3)$$

tion. The complexes are poor conductors in nitrobenzene[10] and each displays a single ν(CO) band in its ir spectrum, shifted to higher frequency. The thiocarbonyl absorption is not shifted to higher frequency, but again appears overlapped with a ligand absorption band near 1095 cm^{-1}, lower than the original CS band by approximately 65 cm^{-1}. These reactions with mercuric halides are in contrast to those reported[11] for *cis*-$W(CO)_2(DPE)_2$ in which ionic products of the type $[W(CO)_2(DPE)_2HgX]HgX_3$ are formed by oxidative addition to the metal.

An ionic,[12] diamagnetic complex is formed in yields above 80% when **1** is stirred with 0.5 equiv of $AgBF_4$ in CH_2Cl_2 or acetone. The thiocarbonyl ν(CS) band can be definitely located in the ir spectrum of this complex and is lowered as compared with that of **1** by about 55 cm^{-1}, while the CO band is raised (Table I). Elemental analyses, molar conductivity, and the stoichiometry of the reaction indicate that two thiocarbonyl molecules are associated with one silver ion, as in eq 4. The carbonyl complex, $W(CO)_2(DPE)_2$,

$$\mathrm{2W(CO)(CS)(DPE)_2 + AgBF_4 \longrightarrow [(DPE)_2(CO)WCSAgSCW(CO)(DPE)_2]BF_4} \qquad (4)$$

in contrast, was found to react with $AgBF_4$ in an oxidation–reduction process with formation of silver metal. The resulting paramagnetic $[W(CO)_2(DPE)_2]BF_4$ was isolated from this reaction, and its identity was confirmed by preparation of the identical complex in a metathesis reaction of the reported triiodide salt[13] $[W(CO)_2(DPE)_2]I_3$ and $AgBF_4$.

Like $(DPE)_2(CO)WCSW(CO)_5$, the mercuric halide and silver ion complexes of **1** are rapidly converted to **1** in CH_2Cl_2 solution in the presence of PPh_3. However, all of these complexes may be recrystallized with very little decomposition occurring in solution.

It is apparent from these studies that in complexes where the electron density on the metal is sufficiently high and the ν(CS) frequency is sufficiently low, the sulfur atom of a thiocarbonyl ligand may act as a donor toward other metals. It is also clear that the sulfur of the CS group in $W(CO)(CS)(DPE)_2$ is a better donor than is the oxygen of the CO. These results indicate that it will be possible to synthesize other complexes containing end-to-end bridging thiocarbonyls.

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(9) $W(CO)(DPE)_2(CS)HgI_2$ crystallizes as the methylene chloride adduct. *Anal.* Calcd for $W(CO)(DPE)_2(CS)HgI_2{\cdot}CH_2Cl_2$: C, 41.45; H, 3.14; S, 2.05. Found: C, 40.98; H, 2.99; S, 1.91.

(10) The molar conductivities of $W(CO)(DPE)_2(CS)HgCl_2$ and $W(CO)(DPE)_2(CS)HgI_2{\cdot}CH_2Cl_2$, *ca.* 10^{-3} *M* in nitrobenzene, are 5.5 and 5.4 ohm^{-1} cm^2 mol^{-1}, respectively.

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B. Duane Dombek, Robert J. Angelici*
Department of Chemistry, Iowa State University
Ames, Iowa 50010

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On the Coupling of Adenosine Triphosphate Hydrolysis to a Simple Inorganic Redox System: $VO^{2+} + H_2O_2$

Sir:

The enzyme-catalyzed hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and inorganic phosphate (P_i) provides the main source of energy for many biological processes. Nonenzymatic hydrolysis of ATP has been investigated by many workers[1-4] in an effort to learn more about the mechanism of catalysis by enzymatic systems. In many biological cases, it appears that ATP hydrolysis occurs simultaneously with some electron transfer reaction. The present work is largely an effort to study catalysis of ATP hydrolysis by a simple inorganic redox reaction (H_2O_2 oxidation of VO^{2+}) in a nonenzymatic system to test a theory that redox reactions mediated by polyphosphates labilize phosphorus to substitution.

Hydrolysis rates of ATP were followed by monitoring the amount of P_i produced, using the molybdenum blue method for phosphate determination as modified by Baginski, *et al.*,[5] for use in the presence of nucleoside phosphates. Standard orthophosphate solutions (with and without added ATP) showed a linear dependence of A_{700} (absorbance of phosphomolybdenum blue complex at 700 nm) with $[P_i]$ giving a slope of $(1.55 \pm 1.07) \times 10^4\ M^{-1}$.

All runs were made using solutions of reagent grade $VOSO_4$, $Na_2H_2ATP \cdot 4H_2O$ (Sigma Chemical Co.), and H_2O_2. Phosphate present buffered the solution to pH ~2.5 in all runs. Only P_i formation was monitored in this preliminary study, but as mentioned below any $P_2O_7^{4-}$ formed would probably be hydrolyzed to P_i by a process similar to that for ATP hydrolysis.

Our initial findings summarized in Table I show comparative rates of hydrolysis of ATP, revealing moderate enhancement by VO^{2+} and dramatic enhancement by coupling with H_2O_2 oxidation of VO^{2+}. Hulett[2] gives a value of $\sim 8 \times 10^{-8}$ sec^{-1} for the first-order rate constant of the uncatalyzed hydrolysis of ATP (at pH 4, 25°). Enhancement of phosphate ester hydrolysis by VO^{2+} alone has also been observed by Hofstetter, *et al.*, in the case of salicylphosphate.[6]

The last two runs in the table indicate that H_2O_2 concentration is an important factor in the enhancement of ATP

Table I. Summary of Catalytic Effects

$[VO^{2+}]_0$, *M*	$[H_2O_2]_0$, *M*	$[ATP]_0$, *M*	Time required for complete hydrolysis (at 25°)
0	0	10^{-2}	>3 months[a]
10^{-2}	0	9×10^{-3}	~8 weeks[a]
0	10^{-2}	10^{-2}	(No enhancement)
10^{-2}	1.2×10^{-2}	9×10^{-3}	1 day
1.3×10^{-2}	1.2×10^{-1}	1.4×10^{-2}	3 hr

[a] Hydrolysis is too slow for accurate measurement of rates.