result in a decrease in the contribution from configuration B in the ground electronic state. The observed difference in the spectral broadening between the $\mathrm{Co^{III}TPP^{\bullet+}}$ and $\mathrm{Co^{III}OEP^{\bullet+}}$ complexes strongly suggests that the ground electronic states of the $\mathrm{Co^{III}OEP^{\bullet+}}$ complexes are of the A_{1u}-dominant type even when they are coordinated by Br^-, Cl^-, or CN^-. Temperature-dependent NMR data for $(\mathrm{Co^{III}OEP^{\bullet+}})(Br^-)_2$ have been explained by the effect of A_{1u}/A_{2u} thermal mixing, but this interpretation must be reexamined by taking into account the effect of configuration B on the NMR spectra.

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High-Pressure Infrared and Micro-Raman Spectra of Crystalline Pentacarbonyl(thiocarbonyl)chromium(0) and (η-Benzene)dicarbonyl(thiocarbonyl)chromium(0)

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Infrared spectra (4300–400 cm^{-1}) of crystalline $Cr(CO)_5(CS)$ and $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$ have been recorded at room temperature for pressures up to 25 and 30 kbar, respectively. High-pressure micro-Raman spectra of $Cr(CO)_5(CS)$ have been similarly investigated in the low-energy region (450–300 cm^{-1}) for pressures up to 25 kbar. The pressure dependences ($d\nu/dP$) of the IR-active, binary ν(CO) overtone and combination modes have been determined and used to calculate the pressure dependences of the parent ν(CO) fundamentals, which could not be determined directly, as these absorptions were hidden by the intense absorption of the diamond windows. There was no evidence of any pressure-induced phase transitions occurring in either complex over the pressure ranges investigated. The $d\nu/dP$ values for the CO and CS stretching modes suggest that in both complexes the π-back-bonding between the Cr and the CO groups is enhanced by increased pressure, while the Cr–CS π-back-bonding is increased for $Cr(CO)_5(CS)$, but the situation is not very clear for $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$. In addition, pressure selectively enhances the π-back-bonding to the CO group trans to CS in $Cr(CO)_5(CS)$.

The pressure dependences ($d\nu/dP$) of the ν(CO) modes in transition-metal carbonyl complexes provide useful information on the extent of π-back-bonding between the metals and the carbonyl groups.[1-7] Since the thiocarbonyl ligand (CS) is considered to be an appreciably better π-acceptor ligand than is CO,[8] we decided to extend our studies to two typical crystalline transition-metal thiocarbonyls, $Cr(CO)_5(CS)$ and $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$, and present here high-pressure IR data for these complexes, together with some high-pressure micro-Raman data for the low-frequency vibrations of the pentacarbonyl derivative.

Experimental Section

The thiocarbonyl complexes were prepared by the literature methods.[9-11] The experimental details for the high-pressure IR and micro-Raman work have been described elsewhere.[1] Raman spectra were recorded using 647.1-nm Kr ion laser excitation.

Results and Discussion

The pressure dependences and relative pressure dependences for the observed IR peaks of $Cr(CO)_5(CS)$ are given in Table I. The absence of any breaks in the slopes of the ν vs P plots up to 25 kbar indicates that there were no pressure-induced phase transitions throughout the pressure range investigated.

Table I. Vibrational Data for $Cr(CO)_5(CS)$

ν, cm^{-1}	$d\nu/dP$, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^2	assignt[a]
4172[b]	0.35	0.0084	$2\nu_1$, A_1
4118[b]	0.40	0.0097	$\nu_1 + \nu_{10}$, B_1
4092[b]	−0.006	−0.0001	$\nu_1 + \nu_2$, A_1
4048[b]	−0.35	−0.0085	$\nu_1 + \nu_{16}$, E
2088	0.18[c]	0.0086	ν_1, a_1, $\nu(CO^{eq})$
2017	0.22[c]	0.011	ν_{10}, b_1, $\nu(CO^{eq})$
2017	−0.18[c]	−0.0089	ν_2, a_1, $\nu(CO^{ax})$
1989	−0.53[c]	−0.027	ν_{16}, e, $\nu(CO^{eq})$
1289	−0.25	−0.019	ν_3, a_1, ν(CS)
1260	−0.09	−0.0072	
636	−0.46 0.33	−0.072 0.052	ν_4, a_1, ν_{17}, e, δ(CrCO)
512	0.16	0.030	ν_{18}, e, δ(CrCO)
487	0.21	0.043	ν_{19}, e, δ(CrCO)
427	0.73	0.17	ν_{20}, e, $\nu(Cr–CO^{eq})$
422	0.82	0.19	ν_5, a_1, $\nu(Cr–CO^{ax})$
381	0.78	0.20	ν_6, a_1, $\nu(Cr–CO^{eq})$
352	0.70	0.20	ν_7, a_1, ν(Cr–CS)

[a] From refs 12, 14, and 15. [b] Data obtained from $Cr(CO)_5(^{13}CS)$. [c] Data derived from overtone and combination bands.

Recent Raman studies have shown that the metal–CO interactions and the molecular geometries of metal carbonyl complexes are particularly sensitive to pressure.[1-7] Unfortunately, in contrast to our earlier work,[1-3] all attempts to record the micro-Raman spectra of $Cr(CO)_5(CS)$ under high pressure in both the ν(CO) and ν(CS) regions failed, because the peaks were inherently too weak to be monitored and extended data accumulation simply resulted in sample decomposition due to the necessary long exposures to the laser excitation. The corresponding IR peaks were quite intense, but an immense absorption due to the diamonds of the DAC completely masked the ν(CO) region. However, the ν(CS) region was free from interference. Also, we discovered that useful high-pressure data could be obtained from the binary ν(CO)

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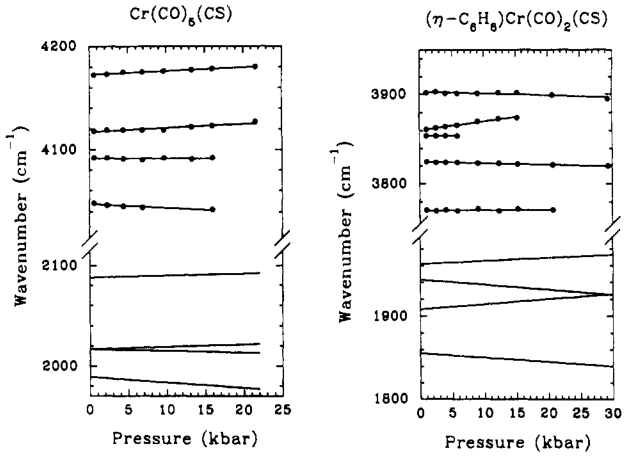

Figure 1. Pressure dependences of the binary ν(CO) overtones and combinations of Cr(CO)$_5$(CS) and (η-C$_6$H$_6$)Cr(CO)$_2$(CS) observed in the IR spectra and calculated values for the ν(CO) fundamentals.

overtone and combinations located in the near-IR region at about 4000 cm^{-1}. On the basis of some near-IR solution work performed earlier,[12] the three bands for Cr(CO)$_5$(^{13}CS),[13] originally located at 4172, 4092, and 4080 cm^{-1} at ambient pressure, can be assigned to $2\nu_1$, $\nu_1 + \nu_2$, and $\nu_1 + \nu_{16}$, respectively. A fourth, relatively strong band at 4118 cm^{-1} (at ambient pressure) was not observed in the solution near-IR study; it has been assigned here to the strictly C_{4v}-symmetry-forbidden $\nu_1 + \nu_{10}$ (B$_1$) combination, which has become allowed in the solid-state spectra due to factor group effects. Normal-coordinate calculations on Cr(CO)$_5$(CS) have shown that ν_{10} and ν_{16} are completely uncoupled from any other modes, ν_1 and ν_2 are slightly mixed, and none of the ν(CO) modes is mixed with ν_3 (CS stretching mode) or any low-energy modes,[14] and the anharmonicity constants associated with ν(CO) modes are quite small.[12] It is reasonable, therefore, to assume that the measured pressure dependences of the binary ν(CO) overtones and combinations (Figure 1) can be equated to the sum of the individual pressure dependences of the two contributing ν(CO) fundamentals. Although there are certainly errors involved in this approximation, the calculated pressure dependences of the four ν(CO) modes of Cr(CO)$_5$(CS) (Table I and Figure 1) are comparable to those for several isomorphous M(CO)$_5$L complexes.[1,3,4] These dν/dP values can be used to discuss qualitatively the effect of pressure on the metal–CO bonding interactions.

The pressure dependences of the ν(CO) modes of metal carbonyls are the net result of two main competing effects. First, compression of the crystal lattice will lead to a shortening of the intramolecular distances and consequently to increase in the vibrational wavenumbers of all the internal modes, including ν(CO). Second, increasing pressure strengthens the π-back-bonding from the metal to the π^* orbitals of the CO groups, resulting in a reduction in the CO bond order and a concomitant decrease in ν(CO). In the case of Cr(CO)$_5$(CS), the slightly positive dν/dP values for ν_1 and ν_{10} and negative values for ν_{16} and ν_2 imply that there is a sufficient increase in the Cr–CO π-back-bonding upon increasing the applied pressure to counteract the opposing lattice compression effect. In addition, a comparison of the dν/dP values for the a$_1$ equatorial CO stretching mode (ν_1) and a$_1$ axial CO stretching modes (ν_2) indicates that pressure selectively enhances the π-back-bonding between the chromium atom and the axial CO group trans to the CS ligand. Replacement of a CO group on Cr(CO)$_6$ by CS leads to a CO force constant for the ν(CO^{ax}) mode which is slightly greater than that for the ν(CO^{eq}) mode.[14,15] Therefore, one of the effects of high pressure on Cr(CO)$_5$(CS) is to diminish the difference between the CO force constants for the two types of CO group.

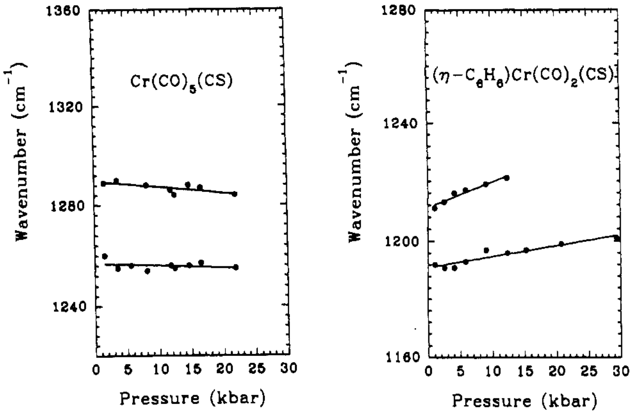

Figure 2. Pressure dependences of the IR-active ν(CS) modes of Cr(CO)$_5$(CS) and (η-C$_6$H$_6$)Cr(CO)$_2$(CS).

Table II. Vibrational Data for the Cr(CO)$_2$(CS) Moiety in (η-C$_6$H$_6$)Cr(CO)$_2$(CS)[a]

ν, cm^{-1}	dν/dP, cm^{-1}/kbar	d ln ν/dP, kbar^{-1} × 10^2	assignt[b]
3902	−0.22	0.0056	1962 + 1943
3861	0.96	0.025	1962 + 1908
3854	0.00	0.000	1943 + 1908
3825	−0.17	−0.0044	1962 + 1856
3771	0.038	0.0010	1908 + 1856
1962	0.37[c]	0.019	ν_1, ν(CO)
1943	−0.59[c]	−0.030	
1908	0.59[c]	0.031	ν_{15}, ν(CO)
1856	−0.54[c]	−0.029	
1211	0.85	0.070	ν_2, ν(CS)
1192	0.37	0.031	
646	0.17	0.026	ν_3, δ(CrCO)
611	0.33	0.054	ν_{16}, δ(CrCO)
600	0.12	0.020	
521	0.21	0.040	ν_5, δ(CrCS)
502	0.28	0.056	ν_{18}, δ(CrCS)
452	0.80	0.18	ν_6, ν(Cr–CO)
432	0.41	0.095	ν_7, ν(Cr–CS)

[a] Similar data for the benzene ring vibrations are available from the authors. [b] From refs 17 and 20. [c] Data derived from overtone and combination bands.

Under D_{2h} factor group symmetry,[16] the a$_1$ CS stretching mode (ν_3) should split into two IR-active components (b$_{2u}$ + b$_{3u}$), and as expected, at ambient pressure, this mode appears as a very broad band centered at 1260 cm^{-1}, with a distinct shoulder at about 1289 cm^{-1}. The broadness of the ν(CS) band results from disorder in the crystal.[16] Both ν(CS) components exhibit negative pressure dependences (Figure 2). These are not, however, simply the result of the competition between lattice compression and π-back-bonding effects. Since there is also appreciable mixing of ν(CS) with the low-energy ν(Cr–CS) mode,[14,15] the large, positive dν/dP value observed for ν(Cr–CS) would be expected to contribute positively to the overall pressure sensitivity of ν(CS). Consequently, the negative pressure dependences found for ν(CS) indicate that it is the π-back-bonding effect that dominates.

Four relatively intense Cr–C stretching modes, ν_7 [ν(Cr–CS), a$_1$], ν_6 [ν(Cr–CO^{eq}), a$_1$], ν_5 [ν(Cr–CO^{ax}), a$_1$], and ν_{20} [ν(Cr–CO^{eq}), e] are observed in the micro-Raman spectra of Cr(CO)$_5$(CS). These four ν(Cr–C) modes have relatively large, positive dν/dP values, consistent with the expectation that the Cr–C bond distances are shortened upon application of pressure.

The pressure and relative pressure dependences of the observed IR bands for the Cr(CO)$_2$(CS) moiety in (η-C$_6$H$_6$)Cr(CO)$_2$(CS)

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are given in Table II. All the bands, especially in the ν(CS) region, are much narrower than those of Cr(CO)$_5$(CS), indicating that the crystal is ordered at ambient conditions. The local symmetry of the Cr(CO)$_2$(CS) moiety is C_s, for which two CO stretching modes (a′ + a″) are expected and observed in the solution IR spectra.[17] In the solid-state IR spectrum (KBr disk), four ν(CO) peaks are detected (Table II). These peak doublings undoubtedly arise from solid-state splitting.

Five binary ν(CO) combination bands, initially at 3902, 3861, 3854, 3825, and 3771 cm^{-1}, were monitored with increasing pressure (Figure 1). These combinations are assigned to 1962 + 1943, 1962 + 1908, 1943 + 1908, 1962 + 1856, and 1908 + 1856 cm^{-1}, respectively. Following the same procedure for Cr(CO)$_5$(CS), we calcualted the pressure dependences of the parent ν(CO) fundamentals (Table II and Figure 1). The negative dν/dP values for certain of these ν(CO) modes again indicate that pressure leads to a significantly strengthening of the π-back-bonding between the metal and the carbonyl groups.

The behavior of the CS stretching region in the high-pressure IR spectra of (η-C$_6$H$_6$)Cr(CO)$_2$(CS) is different from that in Cr(CO)$_5$(CS). Instead of shifting to lower wavenumbers, the strong ν(CS) band, originally positioned at 1192 cm^{-1} (together with an obvious shoulder at 1211 cm^{-1}), moves to higher wavenumber with increasing pressure (Figure 2). Replacement of a CO group in (η-C$_6$H$_6$)Cr(CO)$_3$ by CS leads to an increase in the average CO force constant, but the CS force constant is smaller[17] and the ν(Cr–CS) and δ(CrCS) force constants are greater than those for Cr(CO)$_5$(CS). The CS ligand should, therefore, be a better π-acceptor in the benzene complex than in Cr(CO)$_5$(CS). However, the pressure dependences of the CS stretching modes are positive and dν/dP for the Cr–CS stretching frequency is much smaller, which implies a weaker π-acceptability. This might be due to the interaction between the filled π-bonding orbitals of CS and the filled d orbitals of the metal[18,19] and/or the higher anharmonicity of the thiocarbonyl stretch, both of which would lead to a positive pressure dependence. The high dν/dP values for the Cr–CO stretching modes in (η-C$_6$H$_6$)Cr(CO)$_2$(CS) are consistent with the metal–carbonyl π-back-bonding being enhanced by pressure. There also appears to be no pressure-induced phase transition in this complex.

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Registry No. Cr(CO)$_5$(CS), 50358-90-2; (η-C$_6$H$_6$)Cr(CO)$_2$(CS), 63356-86-5.

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Studies on Gold(II) Complexes with Hard and Soft Donor Ligands. 2.[1] Complexes with *o*-(Methylthio)aniline and 1,2-Bis((*o*-aminophenyl)thio)ethane

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The synthesis and properties of gold(II) complexes with *o*-(methylthio)aniline (Hmta) and 1,2-bis((*o*-aminophenyl)thio)ethane (dae) are reported. *o*-(Methylthio)aniline forms both mononuclear and binuclear complexes depending on the preparative conditions. The isomeric pair of monomeric gold(II) complexes [Au(mta)$_2$Cl]Cl (**1a**,**b**), both of which give a four-line EPR multiplet in CH$_2$Cl$_2$ solution, undergo dimerization in DMF leading to the formation of [Au(mta)$_2$Cl]$_2$Cl$_2$ (**1c**), which exhibits a well-resolved seven-line EPR pattern possibly originating from two ^{197}Au nuclei. The corresponding dimeric bromo (**1d**) and thiocyanato (**1e**) complexes also exhibit similar EPR profiles. A temperature-dependent susceptibility measurement indicates that the two spins are ferromagnetically coupled within the dimer, while a weak antiferromagnetic coupling exists between the dimers. The cyclic voltammetric results are in line with EPR results.

Introduction

Paramagnetic complexes of gold in the formal oxidation state II are very rare,[3–6] and only two monomeric gold(II) complexes with the unsaturated sulfur donor ligands *N*,*N*-dialkyldithiocarbamate (dtc)[3] and maleonitriledithiolate (mnt)[5] are well established.[7–10] In all the reported dimeric complexes[11–21] of gold(II), a strong Au–Au bond is present, and consequently these complexes are diamagnetic. We have reported[1] an isomeric pair of isovalent gold(II) dimeric complexes which give a well-resolved seven-line EPR multiplet originating from two ^{197}Au nuclei ($I = {}^3/_2$) and a monomeric complex of gold(II) with the ligand *o*-aminobenzenethiol (Habt). While continuing our studies on stabilization of the formal oxidation state II for gold by complex formation with hard–soft donor ligands having an extended π-system, we have synthesized and isolated an isomeric pair of monomeric as well as a few dimeric complexes of gold(II) with *o*-(methylthio)aniline (Hmta) and two monomeric gold(II) complexes with 1,2-bis((*o*-aminophenyl)thio)ethane (dae) by the

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