An XPS Study of the Relative π-Acceptor Abilities of the Nitrosyl and Carbonyl Ligands

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The core electron binding energies of $Ni(CO)_4$, $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $Mn(NO)_3CO$, $Cr(NO)_4$, $Fe(CO)_5$, and $Mn(CO)_4NO$ have been determined in order to compare the relative π-acceptor abilities of the NO and the CO groups. The binding-energy trends are roughly consistent with the trends in the C–O and N–O stretching force constants. The data show that back-bonding to a CO group is affected by competitive back-bonding to NO groups bonded to the same metal atom. However back-bonding to an NO group is mainly determined by the nuclear charge on the metal atom and is independent of the number of CO groups, which compete relatively weakly for π-electron density.

Introduction

Because of current interest in catalytic systems involving both NO and CO, the nature of the interaction of these ligands with transition metals is a subject of importance.[1] In order to study the relative abilities of these ligands to withdraw electron density from transition-metal atoms, we have carried out an X-ray photoelectron spectroscopic (XPS) study of two sets of molecules: $Ni(CO)_4$, $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $Mn(NO)_3CO$, and $Cr(NO)_4$; $Fe(CO)_5$ and $Mn(CO)_4NO$. The advantages of studying these particular compounds are as follows: (1) All the compounds are volatile and can be studied in the gas phase. Thus we can avoid the problems (both experimental and interpretive) associated with XPS studies of solids.[2] (2) The compounds in each set are isostructural and isoelectronic. It is a good approximation to assume that, within each set, the electronic relaxation energy associated with the core ionization of a particular type of atom (carbon, nitrogen, or oxygen) is constant on going from one molecule to another.[3] That is, a decrease in core binding energy corresponds to an increase in atomic electron density.

The XPS spectra of frozen samples of $Ni(CO)_4$, $Co(CO)_3NO$, and $Fe(CO)_2(NO)_2$ were previously studied by Barber et al.[4] The accuracy of their measured binding energies was estimated to be ±0.2 eV, in contrast to the typical ±0.05-eV reproducibility of binding energies obtained for gas-phase molecules. We believe our work is an important extension of the earlier work not only because we studied gaseous species (with the corresponding improvement in the quality of the spectra) but also because we completed the study of the isoelectronic series by studying $Mn(NO)_3CO$ and $Cr(NO)_4$. Only in the case of $Mn(NO)_3CO$ was it possible to deconvolute the oxygen 1s spectrum into peaks due to the CO and NO groups. In our study we also obtained data for another isoelectronic system, $Fe(CO)_5$ and $Mn(CO)_4NO$.

From comparisons of N–O and C–O stretching frequencies and force constants in transition-metal nitrosyls and carbonyls, it has been concluded that nitric oxide is only a slightly better π-acceptor ligand than carbon monoxide.[5] On the other hand, ab initio calculations[6] indicate that the metal-atom charges in the series $Ni(CO)_4$, $Co(CO)_3NO$, and $Fe(CO)_2(NO)_2$ are 0.5+, 0.6+, and 1.0+, respectively. If the valence electron density were frozen on going from $Ni(CO)_4$ to $Fe(CO)_2(NO)_2$, the charge on the iron atom would be 2 units more *negative* than that on the nickel atom. Of course, the electron density is not frozen, and the calculations indicate that an enormous amount of electron density is shifted from the iron atom to the ligands by polarization of the metal–ligand bonds. We believe that our XPS data, which allow us to monitor the atomic charges of the CO and NO groups, can give us information about the polarization of the metal–ligand bonds (in particular, the π bonds) and can resolve the question of the relative back-bonding abilities of CO and NO groups.

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Results and Discussion

It has been shown[4,7,8] that, for a wide variety of transition-metal carbonyls, both the carbon 1s and oxygen 1s binding energies are well correlated with the C–O stretching force constants: higher binding energies correspond to higher force constants. The binding energies essentially measure atomic charges; the force constants measure bond strengths. The fact that these entirely different quantities are correlated consistent with the concept of back-bonding (the more back-bonding, the more negative the CO group and the weaker the C–O bond) is strong evidence that both quantities are good measures of back-bonding. It seems reasonable to suppose that nitrogen 1s and oxygen 1s binding energies and N–O force constants can equally well be used to measure back-bonding in the isoelectronic NO^+ ligand. Therefore we shall interpret increases in ligand atom binding energy as evidence for decreased back-bonding and decreases in ligand atom binding energy as evidence for increased back-bonding. The core binding energies of the compounds we studied are listed in Table I. In order to permit comparison with the binding energies, we have included the C–O and N–O force constants in Table I.

The carbon 1s binding energies of $Ni(CO)_4$, $Co(CO)_3NO$, and $Fe(CO)_2(NO)_2$ are essentially identical, but that of $Mn(NO)_3CO$ is significantly higher. The trend in these data is somewhat similar to the trend in the C–O force constant data. Except for the somewhat high value for $Ni(CO)_4$, the C–O force constant is approximately constant on going from $Ni(CO)_4$ to $Fe(CO)_2(NO)_2$ and then rises markedly at $Mn(NO)_3CO$. The nitrogen 1s binding energy decreases gradually on going from $Co(CO)_3NO$ to $Cr(NO)_4$, paralleling the correspoinding steady decrease in the N–O force constant.

We hoped to measure changes in the oxygen 1s binding energies of the CO and NO groups separately. Unfortunately we were unable to resolve the oxygen 1s spectra of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ into two peaks. The O 1s spectrum of $Co(CO)_3NO$, shown in Figure 1, consists of a single, highly symmetric peak. Similarly, the spectrum of $Fe(CO)_2(NO)_2$ consists of a single, slightly broadened peak. Thus in these cases our measured O 1s binding energies are weighted averages of the binding energies of the CO and NO groups. These weighted averages can differ from the individual values for the CO and NO groups by as much as 0.25 eV. In the case of $Mn(NO)_3CO$, the O 1s spectrum is asymmetric and can be deconvoluted into two peaks with an intensity ratio of 1:3, as shown in Figure 2. The deconvoluted peak binding energies are given in Table I. Even if we take account of the uncertainties introduced by using the average oxygen-binding energies for $Co(CO)_3NO$ and $Fe(CO)_2NO)_2$ instead of separate binding energies for the CO and NO groups, it is clear that the oxygen 1s binding energy of the CO groups remains about constant (or decreases slightly) on going from $Ni(CO)_4$ to $Fe(CO)_2(NO)_2$ and then rises markedly at $Mn(NO)_3CO$, as in the case of the carbon 1s binding energy. The oxygen 1s binding energy of the NO groups decreases on going from

Table I. Core Binding Energies and Force Constants

compd	carbon 1s		C–O force const, 10^5 dyn cm^{-1}	nitrogen 1s		N–O force const, 10^5 dyn cm^{-1}	oxygen 1s		metal $2p_{3/2}$	
	E_B, eV	fwhm, eV		E_B, eV	fwhm, eV		E_B, eV	fwhm, eV	E_B, eV	fwhm, eV
Ni(CO)$_4$	293.78 (6)^a	1.11 (14)^a	17.23^b				540.11 (4)	1.43 (10)	861.15 (6)	1.43 (14)
Co(CO)$_3$NO	293.81 (3)	1.13 (7)	17.04^b	407.83 (2)	1.22 (10)	14.44^b	539.99 (3)	1.37 (6)	786.85 (3)	1.32 (8)
Fe(CO)$_2$(NO)$_2$	293.79 (3)	1.10 (7)	17.06^b	407.76 (3)	1.08 (7)	14.12^b	539.91 (2)	1.53 (7)	715.58 (3)	1.25 (8)
Mn(NO)$_3$CO	293.98 (10)	1.17 (6)	17.43^b	407.65 (5)	1.25 (13)	13.75^b	540.47 (6)^c 539.28 (7)^c	1.15 (14)^c 1.26 (10)^c	647.30 (5)	1.30 (13)
Cr(NO)$_4$				407.56 (3)	1.27 (15)	13.33^d	539.46 (4)	1.40 (15)	582.27 (5)	1.32 (15)
Fe(CO)$_5$^{e}	293.71 (5)	1.27 (13)	16.75^f				539.96 (2)	1.38 (5)	715.79 (4)	1.25 (9)
Mn(CO)$_4$NO	293.49 (3)	1.32 (4)	16.65^g	407.77 (8)	1.27 (15)	13.69^g	539.77 (6)	1.55 (5)	647.37 (4)	1.18 (9)

^{a} Uncertainties in the last digit are given in parentheses. ^{b} Force constants taken from: Van Hecke, G. R.; Horrocks, W. D., Jr. *Inorg. Chem.* 1966, 5, 1960. ^{c} The higher binding energy corresponds to the weaker deconvoluted peak, due to the CO oxygen. The lower binding energy corresponds to the NO oxygen. ^{d} Calculated by the method used by Van Hecke and Horrocks, with data of: Swanson, B. I.; Satija, S. K. *J. Chem. Soc., Chem. Commun.* 1973, 40; ref 19. ^{e} The binding energies for Fe(CO)$_5$ have been reported in ref 3. ^{f} The weighted average of the force constants reported by: Haas, H.; Sheline, R. K. *J. Chem. Phys.* 1967, 47, 2996. ^{g} Calculated from the data of Rest and Taylor [Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Chem. Commun.* 1977, 717] by use of methods outlined by Bratermann [Bratermann, P. S. "Metal Carbonyl Spectra"; Academic Press: London, 1975]. The C–O force constant is the average of the axial and equatorial values.
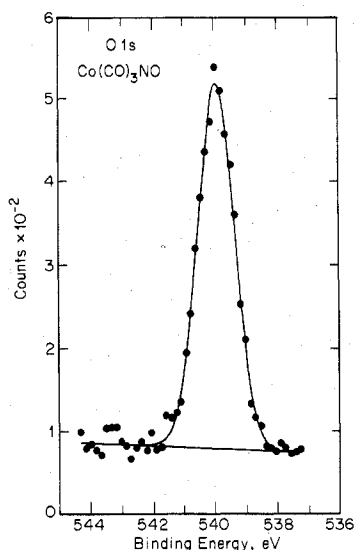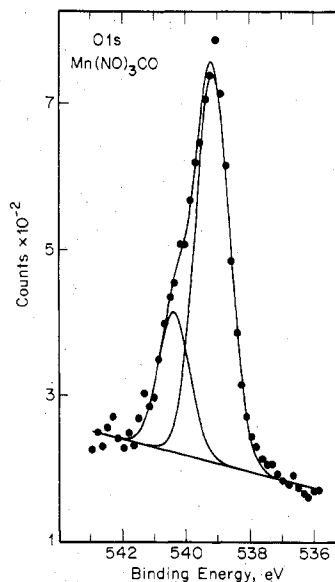

Figure 1. Oxygen 1s spectrum of Co(CO)$_3$NO vapor.

Co(CO)$_3$NO to Mn(NO)$_3$CO and then rises at Cr(NO)$_4$. However, because of uncertainty in the Mn(NO)$_3$CO deconvolution, there is some doubt about the NO oxygen 1s binding energy of Mn(NO)$_3$CO; the NO oxygen 1s binding energies of Mn(NO)$_3$CO and Cr(NO)$_4$ may be closer than indicated by the data in Table I.

On going from Fe(CO)$_5$ to Mn(CO)$_4$NO, both the average carbon 1s binding energy and the average oxygen 1s binding energy decrease, just as one might expect from the decrease in the average C–O force constant.

Except for the small discrepancies noted above, the binding-energy shifts are, within experimental error, in the same directions as the corresponding shifts in the C–O or N–O force constant.

We shall now attempt to interpret the results in terms of simple bonding concepts. The isoelectronic sequence of compounds Ni(CO)$_4$ → Cr(NO)$_4$ can be generated in theory by the successive transfer of protons from the metal-atom nucleus to carbon-atom nuclei. We can think of the isoelectronic pair Fe(CO)$_5$ → Mn(CO)$_4$NO in essentially the same way. On going from one compound to the next in either set, the atomic number of the central metal atom decreases by one unit and a CO group is replaced by a NO group. In each step, the formal charge[9] of the metal atom becomes one unit more negative, and a carbon atom with zero formal charge is replaced by a nitrogen atom with a 1+ formal charge. Therefore we believe that the total amount of negative charge

Figure 2. Oxygen 1s spectrum of Mn(NO)$_3$CO vapor. The points have been fit to two Gaussian curves with intensity ratios of 1:3, corresponding to the CO and NO oxygen atoms, respectively.

transferred from the metal to the four ligands undoubtedly increases on going from Ni(CO)$_4$ to Cr(NO)$_4$ or from Fe(CO)$_5$ to Mn(CO)$_4$NO. The question is: does this shift of electron density occur principally by polarization of the metal–ligand σ bonds (with the charges of the peripheral oxygen atoms changing much less than those of the atoms directly bonded to the metal atoms) or by polarization of the metal–ligand dπ–π* bonds (with the charges of both atoms in each ligand changing to a similar extent)? The correlation between the ligand core binding energies and the ligand stretching force constants can be interpreted, as we have already pointed out, as evidence that the electron flow occurs mainly through the π bonds of the complexes. However, certain features of our binding-energy data independently confirm this interpretation. First, on going through the series from Ni(CO)$_4$ to Cr(NO)$_4$ or from Fe(CO)$_5$ to Mn(CO)$_4$NO, the changes in the oxygen 1s binding energy are at least of the same approximate magnitude as the corresponding changes in either the carbon 1s or nitrogen 1s binding energies. This result is inconsistent with the expected attenuation by the inductive effect of σ-bond polarizations. Indeed, if one considers only the greater σ electronegativity of nitrogen compared to that of carbon, one might have expected the oxygen atoms in Cr(NO)$_4$ to be less negative than those in

Ni(CO)₄, whereas the binding energies indicate the opposite. Second, the oxygen 1s binding energy of the NO ligand is considerably less than that of the CO ligand even when the ligands are attached to the same metal atom (in Mn-(NO)₃CO). This result is indicative of increased back-bonding to the NO ligand. Probably it also reflects the fact that the π* orbital of NO⁺ is distributed relatively evenly between the two atoms, whereas that of CO is somewhat more localized on the carbon atom.[10,11]

The data for Fe(CO)₅ and Mn(CO)₄NO are clearly consistent with our general expectation regarding back-bonding; the carbon 1s and oxygen 1s binding energies and the C–O force constants indicate an increase in back-bonding on going from Fe(CO)₅ to Mn(CO)₄NO. The NO group in Mn(C-O)₄NO occupies an equatorial position,[12] where back-bonding is favored relative to an axial position.[13] For this reason the average back-bonding to the remaining four CO groups might have been expected to be *less* than the average back-bonding to the five CO groups in Fe(CO)₅. The observed increase in back-bonding to the CO groups shows that these ligands are strongly affected by the decrease in the metal-atom nuclear charge but are not obviously affected by the competitive back-bonding to the NO group.

However, the data for the Ni(CO)₄ → Cr(NO)₄ series do show some effects of competition between the NO and CO groups. To rationalize the data, we must assume that the NO groups are much stronger π acceptors than the CO groups. Thus, on going from Ni(CO)₄ to Fe(CO)₂(NO)₂, the back-bonding to the CO groups changes only slightly, because of the strong π-electron withdrawal by the NO groups. In the case of Fe(CO)₂(NO)₂, the metal π-electron density has been depleted so much that, on going another step to Mn(NO)₃CO, the NO groups steal π-electron density from the single remaining CO group, and the back-bonding to CO actually decreases. The data are consistent with a steady increase in back-bonding to the NO groups on going from Co(CO)₃NO to Cr(NO)₄. The back-bonding to the NO groups appears to be determined only by the nuclear charge on the metal atom and to be independent of the number of CO groups, which compete relatively weakly for π-electron density.

The chromium 2p₃/₂ binding energy of Cr(NO)₄ is 0.49 eV greater than that of Cr(CO)₆.[14] Some of this difference may be due to a difference in relaxation energy. However it is probably safe to say that the chromium-atom charge is greater in Cr(NO)₄ than in Cr(CO)₆ even though there are only four ligands in Cr(NO)₄ as opposed to six in Cr(CO)₆. Obviously the transfer of electron density from chromium to the ligands in Cr(NO)₄ is very great.

These systems offer a difficult challenge to theoreticians. We hope that eventually calculations can be made which not only reproduce the XPS data but also can be used to check our interpretations regarding back-bonding. Previous ab initio studies of molecules such as Ni(CO)₄ have not been highly encouraging.[4] For example, the carbon 1s shift between Ni(CO)₄ and free CO was calculated to be 0.3 eV, whereas the actual shift is about 2.5 eV. An approximate MO method[4] gave a shift of 2.1 eV in the wrong direction, i.e., with an error of 4.6 eV.

Experimental Section

XPS Spectra. Gas-phase X-ray photoelectron spectra were obtained by using a GCA/McPherson ESCA 36 spectrometer equipped with an ESCA 36-U gas cell, a magnesium anode, and a cryopump. The experimental procedures and methods for calibrating the spectrometer were the same as those described in a recent paper.[3] The C 1s, N 1s, and O 1s binding energies were measured successfully at least twice; the average deviation from the mean of the runs was less than 0.05 eV in all cases.

Binding energies were determined from the spectra by a least-squares fitting of the points to Gaussian curves.[15] The uncertainties

in the binding energies and fwhm values given in Table I correspond to twice the standard deviations of the least-squares fittings except in a few cases where these values were exceeded by the average deviations of separate runs, in which cases the latter values are given.

The oxygen 1s spectrum of Mn(NO)₃CO was obtained eight times by using three entirely different preparations. In each case the spectrum was asymmetric, with a high-binding-energy shoulder as in the spectrum of Figure 2. The relative intensities of the shoulder and the main peak were similar in all the spectra. The oxygen 1s binding energies reported for Mn(NO)₃CO in Table I are averages of the values obtained by computer deconvolution[15] (assuming a 3:1 intensity ratio for the peaks) from the eight runs. The average deviations from the mean for the CO and NO binding energies are ±0.05 and ± 0.06 eV, respectively.

Compounds. Nickel carbonyl was used as obtained from the Matheson Co. Cobalt tricarbonyl nitrosyl, prepared by the method of King,[16] melted at 0.5–1.5 °C (lit. mp −1 °C). The mass spectrum showed the following peaks (m/e, assignment): 173, Co(CO)₃NO⁺; 145, Co(CO)₂NO⁺; 117, Co(CO)NO⁺; 115, Co(CO)₂⁺; 89, CoNO⁺; 87, CoCO⁺; 59, Co⁺. Iron dicarbonyl dinitrosyl, prepared by the method of King,[16] melted at 17.5–18.5 °C (lit. mp 18 °C). The mass spectrum showed the following peaks (m/e, assignment): 172, Fe(CO)₂(NO)₂⁺; 144, Fe(CO)(NO)₂⁺; 116, Fe(NO)₂⁺; 114, Fe-(CO)NO⁺; 84, FeCo⁺; 56, Fe⁺. Manganese trinitrosyl carbonyl was prepared by the method of Barraclough and Lewis,[17] except that Mn(CO)₅Br (prepared by the method of King[16]) was used as the starting material instead of Mn(CO)₅I. By use of 9.0 g of Mn(CO)₅Br and a reaction temperature of 120 °C, a yield of 0.25 g was obtained. The product was purified on the vacuum line by condensation in a −78 °C trap followed by a 196 °C trap. The compound melted at 27 °C (lit.[17] mp 27 °C). The infrared spectrum (pentane solution) exhibited nitrosyl bands at 1735 and 1822 cm⁻¹ (lit.[17] 1734 and 1823 cm⁻¹) and a carbonyl band at 2088 cm⁻¹ (lit.[17] 2088 cm⁻¹). We were unable to obtain a mass spectrum because of decomposition in the mass spectrometer inlet system. Chromium tetranitrosyl, prepared by the methods of Satija and Swanson[18] and Herberhold and Razavi,[19] melted at 38–39 °C (lit. mp 38–39 °C). The infrared spectrum (pentane solution) exhibited a strong nitrosyl band at 1720 cm⁻¹ (lit. 1721 cm⁻¹). Manganese tetracarbonyl nitrosyl, prepared by the method of King,[16] melted at 0 °C (lit. mp 0 °C). The mass spectrum showed the following peaks (m/e, assignment): 197, Mn(CO)₄NO⁺; 169, Mn(CO)₃NO⁺; 141, Mn(CO)₂NO⁺; 113, Mn(CO)NO⁺; 111, Mn(CO)₂⁺; 85, MnNO⁺; 55, Mn⁺.

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(9) The formal charge of an atom is the charge which the atom would have if the electrons in each bond to that atom were divided equally between the bonded atoms.
(10) The π* orbital of CO is localized 68% on the carbon atom and 32% on the oxygen atom.[11] The π* orbital of O₂²⁺ is symmetrically distributed

between the two atoms. Undoubtedly the delocalization of the π^* orbital of the intermediate isoelectronic species, NO^+, is intermediate between that of CO and O_2^{2+}.

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Characterization of Tantalum Pentachloride Containing Melts by Raman Spectroscopy

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Raman spectroscopy has been used to obtain information on various $TaCl_5$ containing melts. In molten $TaCl_5$, studied between 220 and 350 °C, a gradual dissociation of molecular Ta_2Cl_{10} (D_{2h}) to monomeric $TaCl_5$ (D_{3h}) appears to take place. Evidence for a stable octahedral $TaCl_6^-$ ion in molten $KTaCl_6$ at 420 °C is presented. The binary $TaCl_5$–$AlCl_3$ system at ~200 °C contains noninteracting Ta_2Cl_{10} and Al_2Cl_6 molecules. The complexes formed when $TaCl_5$ is dissolved in $AlCl_3$–NaCl and $AlCl_3$–KCl melts depend on acidity and temperature: $TaCl_6^-$ (O_h) is present only in basic to slightly acidic melts; $TaCl_5$ (D_{3h}) is mainly stable in neutral and acidic melts at high temperature; Ta_2Cl_{10} is found only in acidic melts at lower temperatures.

Introduction

The electrochemistry and coordination chemistry of tantalum(V) dissolved in $AlCl_3$–NaCl melts[2,3] is complex and highly dependent upon temperature and the acidity (pCl⁻) of the melts.[4] This Raman spectral study was undertaken primarily to obtain information on the nature of pentavalent tantalum species in various chloroaluminate melts. Lower valent tantalum compounds are either strongly colored or only sparingly soluble in chloroaluminate melts, making such solutions unsuitable for normal Raman spectroscopy.

Several Ta(V) species may be expected to occur in chloroaluminate melts of varying acidities. Molecular Ta_2Cl_{10} forms the fundamental unit in the solid pentachloride.[5] $TaCl_5$ molecules of D_{3h} symmetry exist in the gas phase at elevated temperatures.[6] Many hexachlorotantalate salts containing the octahedral $TaCl_6^-$ ion are well characterized.[7-9] A $TaCl_4^+$-type complex has not been reported, a fact that is in agreement with the generally accepted strong Lewis acid character of tantalum pentachloride. Neither have chloride-bridged polymeric ions similar to the niobium complex[10] in $SeF_3^+Nb_2F_{11}^-$ been reported.

Experimental Section

The preparation and purification of $AlCl_3$ and NaCl have been described previously.[11] $TaCl_5$ (Alfa) was purified by subliming it five times at 200 °C through a fine Pyrex frit. $KTaCl_6$ was synthesized by melting an equimolar mixture of KCl and $TaCl_5$ at 500 °C. Optical cells were made from square Pyrex tubing (5 × 5 mm). The salts were transferred to the optical cells in an argon-filled drybox (normal H_2O and O_2 content <2 ppm); the cells were evacuated to ~4 μm and sealed. The samples were melted in a furnace made by winding nichrome wire around the square Pyrex tube placed in an insulating block with proper holes for the laser and Raman light. The Raman apparatus has been described previously.[12] Laser lines at 488.0 or 514.5 nm from a Spectra-Physics Model 164 argon-ion laser were used to illuminate the sample. Scattered light was observed at right angles to the exciting beam and polarization measurements were made by rotating the plane of polarization of the illuminating laser light 90°. A modified Cary-81 spectrometer equipped with a cooled EMI 9568 phototube and photon-counting electronics was used to record the spectra. The spectra of molten $KTaCl_6$ and of pure $TaCl_5$ were obtained with 647.1 nm excitation from a Coherent Radiation Model CR 500K krypton ion laser using a JEOL JRS-400D spectrometer.

Results and Discussion

I. Solid and Molten $TaCl_5$. The Raman spectrum of solid $TaCl_5$ at 25 °C (Figure 1a and Table I) was found to be in good agreement with published data,[9] except for additional weak bands at 343, 232, and 146 cm⁻¹ which probably stem from factor-group splittings not resolved previously. Spectral changes on going from solid $TaCl_5$ to the melt at 220 °C (see Figure 1b and Table I) can be attributed to band broadening caused by the higher temperatures. Evidently the structural Ta_2Cl_{10} unit of D_{2h} symmetry shown by X-ray methods to be predominant in the solid state[5] is also the dominating species in low-temperature melts. In the spectra recorded at 300 and 350 °C (Figure 1c,d and Table I) a gradual loss of detail and some minor frequency shifts are observed. The position of the Ta–Cl stretching frequency at 411–414 cm⁻¹ remains, however, virtually the same. The spectrum at 350 °C resembles the spectrum reported by Beattie and Ozin[6] for gaseous $TaCl_5$ which is generally assumed to be a monomeric gas composed of trigonal-bipyramidal D_{3h} molecules. In a similar study by Bues et al.[13] on the endothermic dissociation of molten Nb_2Cl_{10} to liquid $NbCl_5$ considerably larger changes in the Raman spectra were observed in the temperature range 220–320 °C. At least two reasons for this difference between the behavior of molten $NbCl_5$ and $TaCl_5$ can be given: (1) the accidental frequency overlap of the characteristic vibrations of Ta_2Cl_{10} and $TaCl_5$ precludes an estimate of the dimer-to-monomer ratio at a given temperature; (2) it has been shown[14] that $TaCl_5$ is a stronger chloride acceptor than $NbCl_5$ under identical conditions, suggesting that the Ta_2Cl_{10} dimer is more stable than the Nb_2Cl_{10} dimer. We conclude that an endothermic monomerization reaction

$$Ta_2Cl_{10} \rightleftharpoons 2TaCl_5 \tag{1}$$
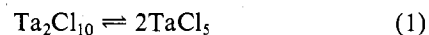
takes place in molten $TaCl_5$, and that higher temperatures ($t > 300$ °C) are needed to dissociate molten Ta_2Cl_{10} than to dissociate Nb_2Cl_{10}.

II. Solid and Molten $KTaCl_6$. $KTaCl_6$ is reported to melt congruently at 410 °C.[15] Evidence for three crystalline modifications has been obtained; the $\gamma \rightarrow \beta$ transition occurs