the glass walls as indicated by the high yields obtained and by the condition of the Vycor tubes after the reactions. Reactions with silicon dioxide of the container seemed to be substantial only if the reaction temperature was above 800° and if the total reaction time exceeded 24 hr.

It seems obvious that the reaction temperature exerts an influence not only on side reactions with the glass walls but also on the main reaction, since the reaction temperature might very well decide which ternary halide is formed as the main product of a conproportionation. This aspect has not been investigated any further, since the preparative efforts were mainly directed at achieving the optimum conditions for the formation of compounds $A_4M_6X_{18}$.

Apart from their significance for the preparation of niobium and tantalum cluster material, conproportionation reactions as those described above should be of general importance for the synthesis of other polynuclear metal cluster halides and, more generally, of ternary halides in very low oxidation states which otherwise might not be easily accessible. Applications of conproportionation reactions to the preparation of $(Mo_6X_8)^{4+}$ and other cluster cations will be described in a later paper.

Acknowledgment. Support of this work by the Youngstown State University Research Council is gratefully acknowledged.

Registry No. $NbCl_5$, 10026-12-7; $NbBr_5$, 13478-45-0; $TaCl_5$, 7721-01-9; $TaBr_5$, 13451-11-1; NaCl, 7647-14-5; KBr, 7758-02-3; Nb, 7440-03-1; Ta, 7440-25-7; $Na_4Nb_6Cl_{18}$, 12766-37-9; $K_4Nb_6Br_{18}$, 12765-98-9; $Na_4Ta_6Cl_{18}$, 51269-65-9; $K_4Ta_6Br_{18}$, 51269-62-6; $Nb_6Cl_{14}\cdot 8H_2O$, 51269-63-7; $Nb_6Br_{14}\cdot 8H_2O$, 51269-60-4; $Ta_6Cl_{14}\cdot 8H_2O$, 51269-64-8; $Ta_6Br_{14}\cdot 8H_2O$, 51269-61-5.

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Spectroscopic Studies of Metal-Metal Bonding. VI. Vibrational Spectra and Analyses of $X_3MFe(CO)_4^-$ (X = Cl, Br; M = Ge, Sn)

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The infrared and laser Raman spectra of the ions $Cl_3GeFe(CO)_4^-$, $Cl_3SnFe(CO)_4^-$, and $Br_3SnFe(CO)_4^-$ are reported, and 16-19 of the 20 expected fundamentals for each ion have been observed and assigned on the basis of C_{3v} symmetry. Vibrational analyses of these spectra and those of the isostructural $X_3MCo(CO)_4$ (M = Ge, Sn; X = Cl, Br, I) have been carried out with a uniform set of approximations. There is close "calculated–observed" agreement while holding the force fields for the $M'(CO)_4$ moiety constant through the respective series and varying only the constants associated with the MX_3 moieties. In each of the three isoelectronic pairs between the two series, $k_{\mathrm{Fe-M}}$ is in a range higher than that for the analogous $k_{\mathrm{Co-M}}$. For $X_3MFe(CO)_4^-$ the metal–metal force constants determined are $k_{\mathrm{Fe-Ge}}(X = Cl) = 1.29 \pm 0.03$, $k_{\mathrm{Fe-Sn}}(X = Cl) = 1.36 \pm 0.03$, and $k_{\mathrm{Fe-Sn}}(X = Br) = 1.10 \pm 0.03$ mdyn/Å. The range of approximation over which this result remains valid and the nature of bonding implications which can be drawn from vibrational analysis of such organometallic compounds are evaluated.

Introduction

In earlier work in this series[1,2] we reported the vibrational spectra and normal-coordinate analysis of several metal-metal bonded cobalt carbonyl compounds of the form $X_3MM'(CO)_4^n$, with $n = 0$; M' = Co; M = Sn, Ge; and X = Cl, Br, I. The primary objective of those studies was to determine the way the metal-metal force constant, $k_{\mathrm{M-Co}}$, depends on the nature of M and X by varying them independently through the series of compounds. In those and other studies[1-5] attention has been drawn to the fact that both σ and π contributions to the M-M' bonding can be important.

Since the nature of the M-M' bonding in these species depends on the relationship of the energies of the available M' (or $M'(CO)_4$) orbitals to those of the MX_3 moiety, it is desirable to be able to vary the M' orbital levels through sets of related compounds. A straightforward method for doing this, and a useful approach to investigating the effect on $k_{\mathrm{M-M'}}$ of varying the participation of the M' orbitals in $X_3MM'(CO)_4^n$ species, while leaving the remainder of the molecule essentially unchanged, is to study the vibrational spectra of isoelectronic molecules.

The iron carbonyl derivatives $X_3MFe(CO)_4^-$ (M = Sn, Ge; X = Cl, Br) are isoelectronic with the $X_3MCo(CO)_4$ molecules studied earlier and, on the basis of 5-μ infrared data, are postulated[6] to be isostructural to them. Formally the difference between these sets of compounds is the isoelectronic replacement of Co(0) by Fe(−I), which causes the M' orbitals to become less stable (higher in energy) relative to MX_3 orbitals than those due to Co(0). The formal result of this is to alter the orbital composition of the $X_3MM'(CO)_4^n$ molecular orbitals and, potentially, to change the relative importance of π bonding in essentially the same manner as that of π^*(CO) orbitals changes through the $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$ series.[7,8] In the latter case, variations in C-O stretching force constants clearly reflect the changes in π^*(CO) participation in the C-O as well as the overall $M(CO)_4$ bonding.

In this paper we report the infrared and laser Raman spec-

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tra and vibrational analyses of $Cl_3GeFe(CO)_4^-$, $Cl_3SnFe(CO)_4^-$, and $Br_3SnFe(CO)_4^-$, and we discuss their bonding in comparison to that of $Cl_3GeCo(CO)_4$, $Cl_3SnCo(CO)_4$, and $Br_3SnCo(CO)_4$.

Experimental Section

The compounds $(C_6H_5)_4AsCl_3SnFe(CO)_4$, $(C_6H_5)_4AsBr_3SnFe(CO)_4$, and $(C_6H_5)_4AsCl_3GeFe(CO)_4$ were prepared in a manner similar to that of Ruff.[6] The reaction mixtures were irradiated until the first signs of turbidity (about 15 min) with a 450-W medium-pressure Hg Hanovia lamp. The residue left after stripping the mixture to dryness was first dissolved in 5 ml of THF before extracting with ether. In all cases the product was sufficiently impure as to require several successive recrystallizations using the sequence THF–ether–pentane. All reagents with the exception of $Fe(CO)_5$ were rigorously prepurified, dried, and degassed before use, and all manipulations were carried out *in vacuo* or under N_2 atmosphere.

The purity of each compound was established by its spectral properties in the 5-μ infrared region, color, and elemental analysis. The analyses, performed by Midwest Microlab, Inc., agreed to within 0.8% of expected values for C, H, X, Fe, and Sn. Sealed capillary and fused-silica cells were used for Raman spectra while KBr or CsI sealed liquid cells and CsI or low-density polyethylene mull plates were used for infrared spectra.

Laser Raman spectra were measured with a Jarrell-Ash 25-300 Raman spectrometer using He–Ne 632.8-nm lasing radiation and constant spectral slit width set between 3 and 5 cm^{-1}. Linearity and accuracy to within 1 cm^{-1} were confirmed by calibration against Ne emission lines.[9] The infrared spectra were measured on Beckman IR-11 and IR-12 spectrophotometers at 2-cm^{-1} resolution and accuracy of better than 1 cm^{-1} as determined by standard resolution tests and wave number calibration.[9,10] A Digilab, Inc., FTS-14 infrared interferometer was also used to measured the spectrum of all samples in the region below 500 cm^{-1} at a resolution of 4- and 1-cm^{-1} accuracy. The Hg arc source in the IR-11 and FTS-14 was filtered with carbon black filled polyethylene to reduce sample decomposition.

Use of the large cation $(C_6H_5)_4As^+$ was mandated by the extra stability such a counterion imparts to the product when in solid form. Suspected coincidences between anion and cation vibrations and the variation in cation band intensities and positions seen when comparing spectra of products and $(C_6H_5)_4AsCl$ necessitated the use of a different cation. The cesium salt of $Cl_3SnFe(CO)_4^-$ was prepared as above except that the photolysis was carried out in THF instead of CH_2Cl_2, and ether was omitted from the purification procedure. The spectra of mulls of $CsCl_3SnFe(CO)_4$ exhibited few coincident absorptions with $(C_6H_5)_4AsCl_3SnFe(CO)_4$ indicating a rather different crystal structure. Solution spectra, however, confirmed the return of the anion to C_{3v} symmetry and helped clear up ambiguities in the regions around 240 and 470 cm^{-1}.

Results

The molecular symmetry of the $X_3MFe(CO)_4^-$ ions studied is assumed to be C_{3v} by direct analogy with the previously reported $X_3MCo(CO)_4$ molecules[1,2] and by the similarities in their vibrational spectra. The vibrational representation for these molecules in C_{3v} symmetry is $\Gamma_{vib} = 9\ A_1$ (ir active, Raman active, polarized) + $2\ A_2$ (inactive) + $11\ E$ (ir active, Raman active, depolarized). Of the 20 predicted infrared- and Raman-active fundamentals, between 16 and 19 have been observed and assigned for each of the compounds discussed here. The observed vibrational spectra of the anions are listed in Table I along with the conditions under which they were obtained and qualitative indications of the intensity and Raman polarization. The bands due to the $(C_6H_5)_4As^+$ cation have been omitted from the table for clarity.

Table I. Observed Infrared and Raman Spectra

Ir freq, cm^{-1}	State	Intens	Raman freq, cm^{-1}	State	Intens	Pol	Symmetry	Assignment
$(C_6H_5)_4AsCl_3GeFe(CO)_4$								
2040	*e*	s	2040	*b*	w		A_1	ν_1
1955	*e*	wm	1953	*b*	m		A_1	ν_2
1935	*e*	wm	1938	*b*	wm		E	ν_{10}
			1919	*b*	wm		E	ν_{10}
620	*e*	s	620	*a*	w	p	A_1	ν_3
529	*d*	m	534	*b*	vw		E	ν_{11}
493	*d*	ms	501	*a*	w	p	A_1	ν_4
			448	*a*	s	p	A_1	ν_5
481	*d*	w					E	ν_{13}
393	*d*	vw					E	ν_{14}
371	*d*	s	378	*a*	m	p	A_1	ν_6
351	*d*	s	358	*a*	wm	dp	E	ν_{15}
254	*d*	w	249	*a*	s	p	A_1	ν_7
			168	*a*	m	dp	E	ν_{16}
164	*d*	s					A_1	ν_8
132	*d*	w	133	*b*	wm		E	ν_{17}
107	*d*	wm	108	*b*	s		E	ν_{18}
			86	*b*	s		E	ν_{19}
54	*d*	m					E	ν_{20}
$(C_6H_5)_4AsCl_3SnFe(CO)_4$								
2036	*a*	s	2033	*a*	w	p	A_1	ν_1
1954	*a*	wm	1951	*a*	wm	p	A_1	ν_2
1937	*a*	vs	1934	*a*	wm	dp	E	ν_{10}
622	*a*	s	621	*a*	w	p	A_1	ν_3
527	*a*	mw	523	*b*	w		E	ν_{11}
493	*a*	ms	493	*a*	wm	p	A_1	ν_4
467	*c*	m					E	ν_{12}
443	*a*	wm	439	*a*	s	p	A_1	ν_5
418	*a*	wm					E	ν_{13}
389	*d*	vw					E	ν_{14}
335	*d*	s	334	*a*	ms	p	A_1	ν_6
315	*d*	s	316	*a*	m	dp	E	ν_{15}
211	*d*	wm	207	*a*	s	p	A_1	ν_7
148	*d*	m					A_1	ν_8
133	*d*	m	136	*b*	s		E	ν_{16}
			121	*b*	s		E	ν_{17}
89	*d*	w	87	*b*	vs		A_1	ν_9
			71	*b*	s		E	ν_{19}
42	*d*	wm					E	ν_{20}
$(C_6H_5)_4AsBr_3SnFe(CO)_4$								
2033	*a*	s	2034	*a*	w		A_1	ν_1
1951	*a*	wm	1955	*a*	wm		A_1	ν_2
1935	*a*	vs	1938	*a*	wm		E	ν_{10}
623	*e*	s	623	*a*	w	p	A_1	ν_3
525	*a*	ms					E	ν_{11}
494	*a*	m	497	*a*	wm	p	A_1	ν_4
443	*a*	wm	443	*a*	ms	p	A_1	ν_5
416	*a*	w					E	ν_{13}
389	*d*	vw					E	ν_{14}
249	*d*	s	247	*a*	wm	p	A_1	ν_6
223	*d*	s	224	*a*	m	dp	E	ν_{15}
185	*d*	m	185	*a*	s	p	A_1	ν_7
122	*d*	w	123	*b*	s		E	ν_{16}
			111	*a*	s		A_1	ν_8
106	*d*	vw					E	ν_{17}
79	*d*	w					E	ν_{18}

[a] THF solution. [b] Solid powder. [c] $CsCl_3SnFe(CO)_4$ in THF. [d] Nujol mull. [e] CH_2Cl_2 solution.

Table II. Symmetries of Vibrational Modes for $X_3MFe(CO)_4^-$ (C_{3v})

C-O str	$2\ A_1 + E$	MX_3 def	$A_1 + 2\ E$
Fe-C str	$2\ A_1 + E$	C-Fe-C def	$A_1 + 2\ E$
Fe-C-O def	$A_1 + A_2 + 3\ E$	M-Fe-C_{ax} def	E
M-X str	$A_1 + E$	Torsion	A_2
Fe-M str	A_1		

Spectral Assignments. The symmetries of the vibrational modes shown in Table II are derived in the usual manner from transformations of the internal coordinates in C_{3v} symmetry. There are three fundamental frequencies in the 2000-cm^{-1} region: two A_1 modes, due to axial and equatorial C-O stretches, and an E mode involving only the equatorial C-O's. Our assignments of the three ν_{CO} fundamentals in

(9) "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," IUPAC Commission on Molecular Spectroscopy, Butterworths, London, 1961.

(10) L. R. Blaine, *J. Res. Nat. Bur. Stand., Sect. C*, 67, 207 (1963).

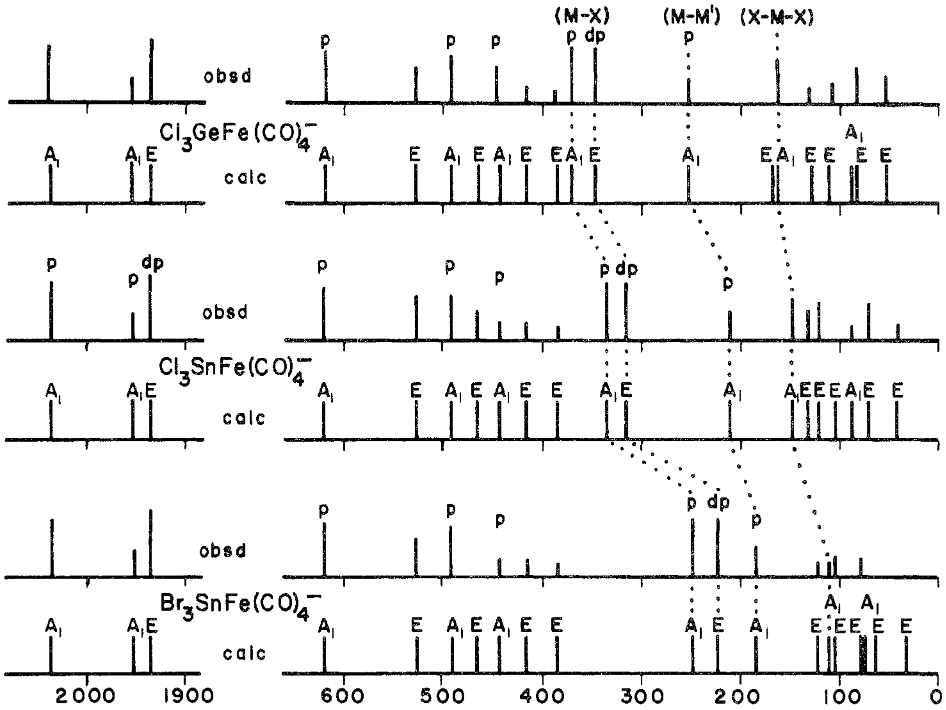

Figure 1. Correlation diagram of observed and calculated fundamentals for the $X_3MFe(CO)_4^-$ series. Results of Raman polarization measurements are shown above the corresponding observed bands and the calculated symmetries above the calculated bands. Bands assigned as predominantly ν_{M-X}, ν_{Fe-M}, and δ_{X-M-X} are also indicated.

this region agree with previous assignments for analogous molecules and are verified by Raman polarization studies and the splitting of the E mode at 1935 cm^{-1} (solution) in the solid state.

On the basis of many studies of metal carbonyl compounds, we expect that the seven active vibrational fundamentals involving Fe-C stretching and Fe-C-O deformation motions will have frequencies in the 350-700-cm^{-1} region. All but one of the fundamentals predicted to occur in the middle frequency region are observed in the infrared spectrum of $Cl_3SnFe(CO)_4^-$. The strong band observed at 622 cm^{-1} is assigned as the A_1 Fe-C-O bending motion out of the equatorial plane. The two other polarized bands (A_1) in this region at 493 and 443 cm^{-1} are assigned as Fe-C axial and Fe-C equatorial stretches, respectively. The remaining bands at 527, 467, and 418 cm^{-1} are assigned as E modes with the band at 527 cm^{-1} expected to be predominantly Fe-C-O bend; the band at 418 cm^{-1} should be predominantly Fe-C equatorial stretch.

For all of the anions studied, the spectra above 400 cm^{-1} are almost identical and therefore the assignements are the same. These bands are all due mainly to motions of the $Fe(CO)_4$ moiety involving very little mixing with other motions.

The three fundamentals, two of A_1 and one of E symmetry, which are largely Fe-M and M-X stretching motions are expected in the 150-400-cm^{-1} spectral region. The infrared spectrum of each of the anions contains a pair of intense absorptions separated by 20-30 cm^{-1} with the higher frequency band of each pair being the narrower. This is the same intensity pattern and spacing seen in the MX_3^- ions,[11] and, although the bands are shifted to higher frequencies with respect to the MX_3^- ions, they are at lower frequencies than the M-X stretches of A_1 and E symmetries found in the corresponding $X_3MCo(CO)_4$ molecules. The symmetry assignment of these metal-halogen stretching bands was confirmed by the polarized Raman spectra.

The strongest band in the Raman spectra in the 150-400-cm^{-1} region of these compounds is polarized and appears at approximately the same frequency as a weak to moderate absorption in the infrared spectra. This band, which is mixed with the A_1 M-X stretching mode, is assigned as the A_1 mode of primarily Fe-M stretching character. This metal-metal stretching mode appears at 254 cm^{-1} in $Cl_3GeFe(CO)_4^-$, 211 cm^{-1} in $Cl_3SnFe(CO)_4^-$, and 185 cm^{-1} in $Br_3SnFe(CO)_4^-$.

The seven remaining bands predicted will consist primarily of MX_3 and C-Fe-C deformations and are expected to appear below 200 cm^{-1}. Because the energy differences between these modes are small, the degree of mixing between modes of the same symmetries is large and an unequivocal description of these modes is specious. Some trends, however, are clearly discernible and are vital in assigning the symmetry of the bands where depolarization ratios were unobtainable due to high background or overlapping bands. The strongest infrared band in this low-frequency region varies in frequency from 164 cm^{-1} in $Cl_3GeFe(CO)_4^-$ to 148 cm^{-1} in $Cl_3SnFe(CO)_4^-$ to 79 cm^{-1} in $Br_3SnFe(CO)_4^-$. This is the same manner in which the MX_3 deformation frequencies are expected to vary for this series of molecules, and the frequencies closely parallel bands assigned as the totally symmetric deformation in corresponding MX_3^- ions[12,13] which are of C_{3v} symmetry. Several other bands vary in frequency in the same way and have been assigned as primarily MX_3 deformation modes. The correlation diagram, Figure 1, highlights variations in the bands assigned as primarily ν_{M-X}, $\nu_{M-M'}$, and symmetric δ_{X-M-X}.

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(12) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968.

(13) J. R. Ferraro, "Low-Frequency Vibrations of Inorganic and Coordination Compounds," Plenum Press, New York, N. Y., 1971.

The E mode corresponding to C(eq)-Fe-C(eq) deformation will not couple strongly with motions of the MX_3 moiety and should show only minor frequency and intensity variations. This mode, which was observed in the 105-120-cm^{-1} region for the $X_3MCo(CO)_4$ series, is expected to occur at slightly higher frequency in this iron carbonyl series due to the greater strength of the Fe-C bond over the Co-C bond. The moderate to strong Raman bands at 133 cm^{-1} in $Cl_3GeFe(CO)_4^-$, 121 cm^{-1} in $Cl_3SnFe(CO)_4^-$, and 122 cm^{-1} in $Br_3SnFe(CO)_4^-$ are therefore assigned as this mode. The remaining observed bands are assigned as a combination of C(ax)-Fe-C(eq) and M-Fe-C(eq) deformations.

These assignments and partial descriptions of the motions involved are given in Table III for the $X_3MFe(CO)_4^-$ series. In this table, the description of each mode is derived from the major calculated potential energy contributions to each mode.

Molecular Valence Force Fields. Although X-ray structural data are lacking for the $X_3MFe(CO)_4^-$ compounds reported here, interatomic distances and angles can be estimated to sufficient accuracy from studies on similar molecules. For the $Fe(CO)_4$ moiety in C_{3v} symmetry the values used for r_{Fe-C} and r_{C-O} were 1.77 ± 0.01 and 1.145 ± 0.005 Å,[14] respectively. The Fe-Sn distance of 2.47 Å and the Fe-Ge distance of 2.37 Å were estimated from metal-metal bond distances reported for other tin- and germanium-substituted iron carbonyls.[14c,15] Parameters used for the MX_3 moiety were estimated from values reported for metal-metal bonded compounds[15,16] where the tin and germanium can be considered in valence state II.

As noted in the spectral assignments, the near identity of the spectra above 400 cm^{-1} indicated that these bands arise from the $Fe(CO)_4$ moiety and that they are little affected by the nature of the MX_3 group. It is therefore reasonable to assume that the molecular force field for the $Fe(CO)_4$ moiety is essentially identical through the series. With this portion of the force field held constant, agreement between the calculated and observed spectra can be obtained by varying only the force field elements for Fe-M stretching, M-X stretching, MX_3 deformation, and their associated interaction constants. This procedure, when applied consistently to closely related molecules, enables one to make firmer conclusions about the bonding than would be possible if the molecular force fields were evaluated independently for each species.

Calculations for this work were carried out using Schactschneider's programs GMAT and VSEC.[17] Symmetry-adapted vibrational coordinates were obtained from the internal coordinates in the usual manner and elements of the symmetrized force field matrix were derived by Jones' method.[18] The initial force field for each member of this series of molecules was transferred directly from that for its $X_3MCo(CO)_4$ analog. Elements involving the $Fe(CO)_4$ moiety were adjusted to fit not only the observed frequencies but also the assigned description of each mode while constraining the individual force field elements to values

Table III. Observed and Calculated Fundamentals

Freq, cm^{-1}		Symmetry	Description
Obsd (ir)	Calcd		
		$Cl_3GeFe(CO)_4^-$	
2040	2037	A_1	$\nu_{C-O(ax)} + \nu_{C-O(eq)}$
1955	1954	A_1	$\nu_{C-O(eq)} + \nu_{C-O(ax)}$
1935	1935	E	$\nu_{C-O(eq)}$
620	621	A_1	$\delta_{Fe-C-O(op)}$
529	529	E	$\nu_{Fe-C(eq)} + \delta_{Fe-C-O(ip)}$
493	493	A_1	$\nu_{Fe-C(ax)}$
	466	E	$\delta_{Fe-C-O(op)}$
448	444	A_1	$\nu_{Fe-C(eq)}$
418	418	E	$\delta_{Fe-C-O(ip)} + \nu_{Fe-C(eq)}$
393	390	E	$\delta_{Fe-C-O(ax)}$
371	371	A_1	$\nu_{Ge-Cl} + \nu_{Fe-Ge}$
351	351	E	ν_{Ge-Cl}
254	254	A_1	$\nu_{Fe-Ge} + \delta_{GeCl_3}$
168	168	E	$\delta_{Cl-Ge-Cl}$
164	164	A_1	$\delta_{GeCl_3} + \nu_{Fe-Ge}$
132	129	E	$\delta_{C-Fe-C} + \delta_{Fe-Ge-Cl}$
108	111	E	$\delta_{C-Fe-C} + \delta_{Ge-Fe-C(eq)}$
	89	A_1	$\delta_{C-Fe-C(ax)} + \nu_{Fe-Ge}$
86	87	E	$\delta_{C-Fe-C} + \delta_{Fe-Ge-Cl}$
54	53	E	$\delta_{Ge-Fe-C} + \delta_{Fe-Ge-Cl}$
		$\lvert\nu_{obsd} - \nu_{calcd}\rvert_{av} = 1.2\ cm^{-1}$	
		$Cl_3SnFe(CO)_4^-$	
2036	2036	A_1	$\nu_{C-O(ax)} + \nu_{C-O(eq)}$
1954	1954	A_1	$\nu_{C-O(eq)} + \nu_{C-O(ax)}$
1937	1936	E	$\nu_{C-O(eq)}$
622	622	A_1	$\delta_{Fe-C-O(op)}$
527	527	E	$\nu_{Fe-C(eq)} + \delta_{Fe-C-O(ip)}$
493	493	A_1	$\nu_{Fe-C(ax)}$
467	467	E	$\delta_{Fe-C-O(op)}$
443	443	A_1	$\nu_{Fe-C(eq)}$
418	418	E	$\delta_{Fe-C-O(ip)} + \nu_{Fe-C(eq)}$
389	390	E	$\delta_{Fe-C-O(ax)}$
335	335	A_1	$\nu_{Sn-Cl} + \nu_{Fe-Sn}$
315	315	E	ν_{Sn-Cl}
211	211	A_1	$\nu_{Fe-Sn} + \delta_{SnCl_3}$
148	148	A_1	δ_{SnCl_3}
133	133	E	$\delta_{Cl-Sn-Cl}$
121	122	E	$\delta_{C-Fe-C} + \delta_{Fe-C-O}$
	105	E	$\delta_{C-Fe-C} + \delta_{Sn-Fe-C(eq)}$
89	88	A_1	$\delta_{C-Fe-C(ax)} + \nu_{Fe-Sn}$
71	71	E	$\delta_{Sn-Fe-C} + \delta_{C-Fe-C}$
42	43	E	$\delta_{Fe-Sn-Cl} + \delta_{Sn-Fe-C}$
		$\lvert\nu_{obsd} - \nu_{calcd}\rvert_{av} = 0.3\ cm^{-1}$	
		$Br_3SnFe(CO)_4^-$	
2033	2036	A_1	$\nu_{C-O(ax)} + \nu_{C-O(eq)}$
1951	1953	A_1	$\nu_{C-O(eq)} + \nu_{C-O(ax)}$
1935	1935	E	$\nu_{C-O(eq)}$
623	622	A_1	$\delta_{Fe-C-O(op)}$
525	527	E	$\nu_{Fe-C(eq)} + \delta_{Fe-C-O(ip)}$
494	491	A_1	$\nu_{Fe-C(ax)}$
	467	E	$\delta_{Fe-C-O(op)}$
443	444	A_1	$\nu_{Fe-C(eq)}$
416	418	E	$\delta_{Fe-C-O(ip)} + \nu_{Fe-C(eq)}$
389	390	E	$\delta_{Fe-C-O(ax)}$
249	249	A_1	$\nu_{Sn-Br} + \nu_{Fe-Sn}$
223	223	E	ν_{Sn-Br}
185	185	A_1	$\nu_{Fe-Sn} + \nu_{Sn-Br}$
122	122	E	$\delta_{C-Fe-C} + \delta_{Fe-C-O}$
111	111	A_1	$\delta_{SnBr_3} + \delta_{C-Fe-C(ax)}$
106	105	E	$\delta_{C-Fe-C} + \delta_{Sn-Fe-C(eq)}$
79	79	E	$\delta_{Br-Sn-Br}$
	76	A_1	$\delta_{C-Fe-C(ax)} + \delta_{SnBr_3}$
	65	E	$\delta_{Sn-Fe-C} + \delta_{SnBr_3}$
	32	E	$\delta_{Fe-Sn-Br}$
		$\lvert\nu_{obsd} - \nu_{calcd}\rvert_{av} = 1.1\ cm^{-1}$	

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comparable with other metal carbonyls.[1,18-20] Three interaction constants not used in the $X_3MCo(CO)_4$ series were introduced to accomplish this while three elements used in that series were set to zero.[21]

Only eight force field elements were permitted to vary through the series while the rest of the force field was being adjusted. The variable elements are k_{Fe-M}, $k_{Fe-M,M-X}$, and three diagonal elements and direct interactions associated with the MX_3 moiety. All but two of the modes below 400 cm^{-1} are strongly dependent (30-98%) on these variable force field elements. The number of possible solutions to the secular equation is limited by restricting the range of the variable force field elements to be in reasonable correlation with the force constants determined for more completely characterized molecules such as the group IVa tetrahalides.[22] Another obvious constraint is that the calculated eigenvectors of each band describe the motion to which each of the bands in the observed spectrum was assigned.

In force fields where the off-diagonal elements (interaction constants) are about an order of magnitude less than their associated diagonal elements, the bands in the 150-400-cm^{-1} region are largely determined by the three force constants k_{Fe-M}, k_{M-X}, and $k_{Fe-M,M-X}$. The variation of $k_{M-M'}$ with k_{M-X} has been shown[1] to describe an ellipse tilted so that its major axis has a negative slope. In such an ellipse the extremal values of $k_{M-M'}$ and k_{M-X} correspond to force fields where one of the two A_1 modes in the 150-400-cm^{-1} region shows complete separation of the M-M' from the M-X stretching motions. From band shapes, intensities, and depolarization ratios the higher frequency A_1 band in this region has been assigned as M-X stretch and the lower frequency band as Fe-M stretch. In the elliptical variation of k_{Fe-M} with k_{M-X}, this description results when either k_{M-X} is at its maximum or k_{Fe-M} is at its minimum. (At the other two extremal values, the higher frequency A_1 band is predominantly Fe-M stretch.) At the k_{Fe-M} minimum, the lower frequency is predominantly ν_{Fe-M} with no ν_{M-X} contribution and the higher frequency is largely ν_{M-X}.

To facilitate comparisons of metal-metal bond strength, the variable force field elements were adjusted as in the Co series until k_{Fe-M} was at its minimum. The ellipse segments of greatest interest are shown in Figure 2. In the region k_{Fe-M}(minimum) + 0.06 mdyn/Å, the band assigned as ν_{Fe-M} retains that description in the calculations while ν_{M-X} varies from 0 to 10% contribution to the total potential energy of the mode. There are contributions from motions of the $Fe(CO)_4$ moiety to ν_{Fe-M}, but these contributions are virtually constant for a given molecule over all reasonable values of the $Fe(CO)_4$ portion of the force field.

The only other contributions of real significance to ν_{Fe-M} arise from k_{X-M-X}, k_{Fe-M-X}, and $k_{Fe-M,Fe-M-X}$. The symmetrized diagonal force field element involving k_{Fe-M-X} was kept constant for the series in the A_1 modes because of its redundancy with k_{X-M-X}. The value of k_{X-M-X} affects the magnitude of k_{Fe-M} according to the degree of mixing of δ_{X-M-X} with ν_{Fe-M}. This mixing is least for $Br_3SnFe(CO)_4^-$ and greatest in $Cl_3GeFe(CO)_4^-$. There is, however, only one solution using realistic values for the four effectively variable force constants which describes ν_{M-X}, ν_{Fe-M}, and δ_{X-M-X} as assigned and which makes the contribution of ν_{M-X} to ν_{Fe-M} zero when k_{Fe-M} is at its minimum value. Diagonal elements of the molecular valence force field and all variable elements are given in Table IV (see paragraph at end of paper regarding supplementary material). The calculated frequencies reported in Table III are from force fields where k_{Fe-M} is at its minimum. The loci of points in Figure 2 are from force fields which give $|\nu_{calcd} - \nu_{obsd}|_{av} < 2$ cm^{-1} in all cases. The optimum ranges of metal-metal force constants found for $X_3MFe(CO)_4^-$ are $k_{Fe-Ge}(X = Cl) = 1.29 \pm 0.03$, $k_{Fe-Sn}(X = Cl) = 1.36 \pm 0.03$, and $k_{Fe-Sn}(X = Br) = 1.08 \pm 0.01$ mdyn/Å.

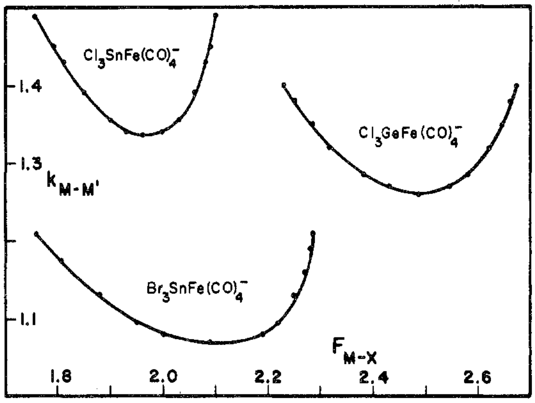

Figure 2. The variation of k_{Fe-M} with F_{M-X} ($k_{M-X} + 2k_{MX,MX}$) for the three molecules. Force fields corresponding to points on these elliptical segments give calculated spectra whose band positions and descriptions are in excellent agreement with those observed and assigned.

Discussion

The major reason for performing a complete vibrational analysis on these molecules is to compare the force field obtained for the $X_3MFe(CO)_4^-$ series with that of the previously reported[1,2] $X_3MCo(CO)_4$ series of molecules. In particular, it is of interest to compare the values of the metal-metal stretching force constant and to determine the bonding implications of the results. There are three important relationships between the metal-metal force constants found for the $X_3MM'(CO)_4^n$ series: (a) $k_{Fe-M} > k_{Co-M}$ for analogous MX_3 derivatives, (b) $k_{M'-SnX_3} > k_{M'-GeX_3}$, and (c) $k_{M-M'}(X = Cl) > k_{M-M'}(X = Br) > k_{M-M'}(X = I)$. Force constants other than $k_{M-M'}$ correlate well with their analogs in simpler molecules and reflect the chemistry of metal carbonyls and metal halides, but even without such restrictions the same trends are found in the metal-metal force constants. For example, in a recent iterative calculation by Devarajan and Cyvin[23] on $Cl_3MCo(CO)_4$ (M = Si, Ge, Sn), the values found for k_{Co-M} were essentially the same as those reported in ref 2 although the calculation gave relative values of $k_{Co-C(eq)}$ and $k_{Co-C(ax)}$ contrary to that expected from dπ-pπ Co-C bonding considerations and gave an ordering of k_{M-Cl} values inconsistent with simple metal chloride spectra.

The key conclusion from the present study is that the Fe-M

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(21) Vibrational analyses of the $X_3MCo(CO)_4$ series using the same basis interactions and similar assumptions as in the $X_3MFe(CO)_4^-$ series require changes in only three diagonal elements per molecule previously reported: $k_{C-O(eq)} = 2.54$, $k_{Co-C-O(ip)} = 0.30$, $k_{Ge-Cl} = 2.10$, $k_{Ge-Br} = 2.05$, $k_{Ge-I} = 1.94$, $k_{Sn-Cl} = 2.12$, $k_{Sn-Br} = 1.84$, and $k_{Sn-I} = 1.71$. The complete force field used in this calculation is included in the microfilm edition of this paper. (See paragraph at end of paper regarding supplementary material.)

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Table IV. Valence Force Field Elements[a] for $X_3MFe(CO)_4^-$

Diagonal Elements Held Constant

$k_{C-O(ax)}$	16.55	$k_{Fe-C-O(eq,op)}$	0.30
$k_{C-O(eq)}$	15.26	$k_{Fe-C-O(eq,ip)}$	0.31
$k_{Fe-C(ax)}$	2.57	$k_{C-Fe-C(ax)}$	0.16
$k_{Fe-C(eq)}$	2.58	$k_{C-Fe-C(eq)}$	0.09
$k_{Fe-C-O(ax)}$	0.30	$k_{M-Fe-C(eq)}$	0.09

Elements Which Vary

	$Cl_3GeFe(CO)_4^-$	$Cl_3SnFe(CO)_4^-$	$Br_3SnFe(CO)_4^-$
k_{Fe-M}	1.26 (1.29 ± 0.03)	1.33 (1.36 ± 0.03)	1.07 (1.10 ± 0.03)
k_{M-X}	1.82 (1.82 ± 0.05)	1.66 (1.66 ± 0.04)	1.54 (1.53 ± 0.06)
$k_{M-X,M-X}$[b]	0.33 (0.33 ± 0.04)	0.15 (0.14 ± 0.04)	0.28 (0.27 ± 0.06)
$k_{Fe-M,M-X}$[b]	0.38 (0.39 ± 0.17)	0.19 (0.21 ± 0.15)	0.29 (0.28 ± 0.14)
k_{X-M-X}	0.25	0.16	0.12
$k_{X-M,X-M-X}$[b]	0.05	0.01	0.02
k_{Fe-M-X}	0.07	0.03	0.03
$k_{Fe-M-X,Fe-M-X}$[b]	−0.02	0.00	0.00

[a] All force constants in mdyn/Å. Abbreviations: ax, axial; eq, equatorial; op, bend out of equatorial plane; ip, bend in equatorial plane.
[b] Off-diagonal element (interaction constant).

bond is as strong or stronger than its Co-M analog. This result is best explained by treating the essential difference between the two series as the formal isoelectronic replacement of Co(0) by Fe(−I). Although the iron may be considered formally zerovalent since the synthesis of $X_3MFe(CO)_4^-$ proceeds by photolytic cleavage of a CO from $Fe(CO)_5$ and substitution with MX_3^-, a negative charge on iron is stabilized by the presence of carbonyl groups as in $Fe(CO)_4^{2-}$. Indeed, the trend in metal-halogen stretching frequencies shown in Table V implies that the oxidation state of the group IV metal in the $X_3MFe(CO)_4^-$ series is intermediate between the M(II) of MX_3^- and M(IV) of MX_4 which is the reactant in the preparation of $X_3MCo(CO)_4$.

The metal-metal σ bond in isoelectronic $X_3MM'(CO)_4^n$ species is postulated to be formed from combinations in A_1 symmetry of the lowest unoccupied level of $Fe(CO)_4$ (or $Co(CO)_4^+$), an A_1 orbital of primarily d_{z^2} character, and the highest occupied level of MX_3^-, either an sp^3 hybrid or a predominantly d_{z^2} orbital. A molecular π-type orbital between the metals can be formed from the degenerate (E) pairs of metal valence orbitals nd_{xz}, nd_{yz}, and $(n + 1)p_x$, $(n + 1)p_y$ which are of the correct symmetry for π overlap and bond formation, although only the d orbitals are formally filled.

The basic atomic orbitals localized on Fe(−I) will be higher in energy than those on isoelectronic Co(0), and the Co-M σ bond is expected to be stronger than the Fe-M σ bond. Our vibrational analysis shows, however, that $k_{Fe-M} > k_{Co-M}$ so other effects need to be considered. In particular, the formal replacement which alters the energy levels of $Fe(CO)_4^-$ relative to MX_3 changes the relation between the orbitals available for π M-M' bonding as well as the σ energy levels. Raising the M' levels on going from Co(0) to Fe(−I) brings the occupied π-type orbitals closer in energy to the vacant MX_3 π levels, and Fe-M π bonding is correspondingly greater than Co-M π bonding. This effect is apparently pronounced enough to more than offset the decrease in σ-bond strength.

This interpretation is consistent with the other force constants found for the molecules. Since changes in k_{C-O} reflect primarily changes in the π*(CO) population and since this force constant is significantly less in the $Fe(CO)_4$ moiety than in $Co(CO)_4$, the dπ-pπ overlap is enhanced when going from Co to Fe. Conversely, k_{Fe-C} is greater than k_{Co-C} as expected. For both series of molecules, $k_{C-O(ax)} > k_{C-O(eq)}$ and $k_{M'-C(ax)} < k_{M'-C(eq)}$ implying that there is less back-donation to the axial CO than to the equatorial CO's. Such a result follows if there is preferential dπ donation to the axial MX_3 orbitals. In the same manner as the metal-carbon force constants, $k_{Fe-M} > k_{Co-M}$ primarily because of increases in the degree of π bonding, and this greater degree of Fe-M π bonding reduces the effectiveness of metal-halogen π bonding relative to the cobalt series analogs and is reflected in the lower values of k_{M-X} in the iron series.

Table V. Variation of M-X Stretching Frequency[a]

	MX_3^- $\nu_1(a_1)$[b]	$X_3MFe(CO)_4^-$ ν_{M-X} (a_1)	$X_3MCo(CO)_4$ ν_{M-X} (a_1)[c]	MX_4 ν_1 (a_1)[b]	MX_4 ν_3 (t_2)[b]
Ge-Cl	320	371	391	397	451
Sn-Cl	297	335	365	368	403
Sn-Br	211	249	261	222	281

[a] All values in cm^{-1}. [b] Values from ref 13. [c] Values from ref 1 and 2.

The greater strength of metal-tin bonds relative to analogous metal-germanium bonds is commonly observed. For example, a mass spectral study[24] of the series $(\pi\text{-}C_5H_5)(CO)_3M'MMe_3$ (M' = Cr, Mo, W; M = Ge, Sn) determined that the M'-Sn dissociation energies are greater than in the M'-Ge derivatives. As discussed above, this may be explained by considering the relation between the M' and M π levels. In the previously reported $X_3MCo(CO)_4$ series, steric and inductive effects were found to rationalize differences in the metal-metal bonds. The surprising strength of iron-metal bonds relative to their isoelectronic cobalt-metal analogs, however, implies the presence of partial multiple bonding between the metals in these compounds.

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Registry No. $(C_6H_5)_4AsCl_3GeFe(CO)_4$, 51269-33-1; $(C_6H_5)_4AsCl_3SnFe(CO)_4$, 51266-69-4; $(C_6H_5)_4AsBr_3SnFe(CO)_4$, 51266-71-8; $Cl_3GeFe(CO)_4^-$, 51269-32-0; $Cl_3SnFe(CO)_4^-$, 51266-68-3; $Br_3SnFe(CO)_4^-$, 51266-70-7.

Supplementary Material Available. A listing of complete valence force fields at the $k_{M-M'}$ minimum for the $X_3MM'(CO)_4^n$ series will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from

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this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1702.

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Chloro Complexes in Molten Salts. II.[1] Potentiometric and Spectrophotometric Study of Chloro Complexes Formed in KCl-AlCl$_3$-TeCl$_4$ at 300°

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The chloro complexes existing in the pCl$^-$ range from 0.28 to 3.84 in KAlCl$_4$ at 300° were found both by potentiometric and spectrophotometric measurements to be TeCl$_6^{2-}$, TeCl$_5^-$, TeCl$_4$, and TeCl$_3^+$. The p*K* values based on molar concentrations for the reactions TeCl$_6^{2-}$ $\rightleftharpoons$ TeCl$_5^-$ + Cl$^-$, TeCl$_5^-$ $\rightleftharpoons$ TeCl$_4$ + Cl$^-$, and TeCl$_4$ $\rightleftharpoons$ TeCl$_3^+$ + Cl$^-$, were found to be in the regions 0.68–0.82, 2.13–2.32, and 3.66–3.92, respectively. The spectra of TeCl$_6^{2-}$, TeCl$_5^-$, TeCl$_4$, and TeCl$_3^+$ were calculated on the basis of the found equilibrium constants. Assuming that the composition of the precipitate at low pCl$^-$ is K$_2$TeCl$_6$, the concentration of TeCl$_6^{2-}$ in a KAlCl$_4$ melt saturated with this precipitate at 300° was calculated to be in the range 0.159–0.177 *M*.

Introduction

Some predictions about the possible chloro complexes of tetravalent tellurium were given earlier.[2,3] Since then it has been shown that it is possible with the use of a chlorine–chloride electrode to treat quantitatively what are essentially acid-base equilibria in a chloroaluminate melt.[1] By means of this electrode and by means of spectrophotometric measurements it has been possible to identify and describe some of the chloro complexes formed.

Not much is known about tellurium complexes in melts, but by means of conductometric titrations[4] a 2:1 compound of KCl and TeCl$_4$ in molten SbCl$_3$ has been shown to exist. This is consistent with the formation of a TeCl$_6^{2-}$ ion. From phase diagrams of MCl-TeCl$_4$ (M = Li, Na, K, Rb, Cs), the solid compounds with overall composition M$_2$TeCl$_6$ (M = K, Rb, Cs) and MTeCl$_5$ (M = Rb, Cs) are known to exist.[5] The phase diagram of the TeCl$_4$-AlCl$_3$ system shows that a 1:1 compound is formed.[6] Raman spectra of both the liquid and the solid state indicate that the compound formed consists of TeCl$_3^+$ and AlCl$_4^-$.[7] Also, compounds like (TeCl$_3$)-AsF$_6$ are known to exist and the molecular weight of this compound in high dilution in nitrobenzene agrees with the above formula.[8] The structure of molten TeCl$_4$ is still unknown although several proposals have been put forward. However, solid TeCl$_4$ is known[9] to consist of Te$_4$Cl$_{16}$ units. From this it was anticipated that both monomeric and polymeric tellurium complexes might be present in the chloroaluminate melt.

Experimental Section

Materials and Measurements. AlCl$_3$ was made from the pure metal (99.999%) and HCl gas (electronic grade from Matheson). KCl (analytical reagent from Riedel-de Haen) was purified by first passing HCl gas over the solid and then through the melt, flushing with pure N$_2$, and finally filtering the melt.[10,11] The TeCl$_4$ was made by reaction between tellurium (99.999%) and chlorine (Fluka, >99.9%).

The experimental techniques used in the present work are almost the same as those described previously.[1,12] The electrode cells were made of Pyrex with vitreous carbon rods from Carbone–Lorraine fused into the bottom. Chlorine (Fluka, >99.99%) was added under a known pressure to the cells, which were sealed vacuum-tight. A sintered disk from Radiometer separated the two cell compartments. This disk consisted primarily of α-Al$_2$O$_3$; it was considered to be satisfactorily mounted if the leak under a water pressure of 300 mm did not exceed 0.2 cm^3 of water over a 12-hr period. In order to secure the same pressure over the melt in both compartments they were connected by a small tube. The internal resistances of the operating cells were usually in the range 100–500 Ω. Furthermore, the electrodes had completely recovered within the experimental uncertainty of ±0.1 mV within about 30 sec after a removal of potential of 20 mV applied for 1 min. On the basis of this the electrodes were considered to be reversible.

The temperature of the main part of the potentiometric furnace was controlled by a Eurotherm regulator, Type LP96/CR/DHS/PID/FC, connected to a platinum resistance thermometer. The top and bottom heating elements were controlled by a simple regulator, Type LP96/MK2/PID/FC, operated by the small temperature difference measured by thermocouples placed on the middle and end part of the furnace. The temperature could be controlled within ±0.1° in the range 100–500°. The temperature variation over the middle 200 mm of the furnace was less than 0.3°. The temperature of the furnace was measured by a calibrated chromel–alumel thermocouple connected to a Type DM2022S digital voltmeter from Digital Measurements Ltd. with a built-in standard cell. The same instrument was also used for the potentiometric measurements.

The optical cells were of fused quartz (Ultrasil from Helma) and had a fixed path length in the range 10–1 mm. A path length around 0.1 mm could be obtained by placing a precision-ground fused-silica insert into a 5-mm cell. Absorption spectra were measured with a Cary 14R spectrophotometer equipped with a furnace regulated by an Eurotherm regulator, Type LP96/DHS/PID/P. The spectro-

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