Journal of Organometallic Chemistry, 349 (1988) 383–391
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The vibrational spectra of t-butyl isocyanide and the homoleptic cations $[M(CNCMe_3)_6]^{n+}$ (M = Re, *n* = 1; M = Ru and Os, *n* = 2) as their hexafluorophosphate salts

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(Received February 1st, 1988)

Abstract

Infrared and Raman spectra have been recorded for liquid t-butyl isocyanide and, with the aid of polarization data, a complete vibrational assignment proposed on the assumption of C_{3v} symmetry for the molecule. Solid state infrared and Raman spectra have also been obtained for the homoleptic complexes $[M(CNCMe_3)_6](PF_6)_n$ (M = Re, $n = 1$; M = Ru and Os, $n = 2$), together with solution data for the $\nu(N{\equiv}C)$ region of the three complexes. Fundamental vibrations have generally been assigned by assuming local O_h symmetry for the $M(CNC)_6$ moieties and for the PF_6^- anions. Approximate NC force constants have been calculated and related to the σ-donor, π-acceptor capabilities of Me_3CNC when ligated to Re^I, Ru^{II} and Os^{II}. Anomalous relative intensities of the Raman-active A_{1g} and E_g $\nu(NC)$ bands have been noted.

Introduction

Although t-butyl isocyanide has been widely employed as a ligand in both coordination and organometallic chemistry, it is surprising to find that, apart from a record of the infrared $\nu(N{\equiv}C)$ frequency [1], no vibrational spectroscopic data have been published for this compound. However, the vibrational spectra of several other t-butyl compounds Me_3CX, (X = e.g. H [2] halogen [3–5], C≡CH [6], and C≡N [7,8]) have been reported. Of these, t-butyl cyanide clearly should provide the most useful comparison with the isocyanide. However, assignments proposed in the two most

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0022-328X/88/$03.50

detailed studies [7,8] of the cyanide show significant differences, even with the benefit of Raman polarisation data. Thus, assignments for the C–H stretches, CH_3 asymmetric and symmetric deformations and the CC_3 deformations are quite different, so the two studies are not as helpful in assigning the vibrational bands of the isocyanide as anticipated.

The microwave spectrum of t-butyl isocyanide has been investigated [9] and is typical of a symmetric rotor, so it was felt worthwhile to examine the infrared and Raman spectra of this compound. The spectroscopic assignments have then been applied to a study of the vibrational spectra of the octahedral homoleptic isocyanide complexes $[Re(CNCMe_3)_6]PF_6$, $[Ru(CNCMe_3)_6](PF_6)_2$ and $[Os(CNCMe_3)_6](PF_6)_2$. Vibrational spectroscopic data on most metal isocyanide complexes have in the past been limited to a listing of the infrared-active $\nu(N{\equiv}C)$ frequencies, although a few more comprehensive studies have been reported [10]. Studies of $[Mn(CNR)_6]^{n+}$ (R = alkyl, aryl; $n = 1, 2$) [11] and $Re_2(CO)_{10-n}(CNR)_n$ (R = Me, t-Bu or $PhCH_2$; $n = 1$–3) [12] have been published recently, and are especially pertinent in that t-butyl isocyanide-metal complexes are included.

Experimental

t-Butyl isocyanide (Fluka AG) was redistilled before use. The complexes $[Re(CNCMe_3)_6]PF_6$, $[Ru(CNCMe_3)_6](PF_6)_2$ and $[Os(CNCMe_3)_6](PF_6)_2$ were prepared as before [13,14].

Infrared spectra of liquid Me_3CNC, and of mull and solution spectra of the three metal complexes in the region 4000–200 cm^{-1} were recorded with a Perkin–Elmer 599B spectrophotometer. Low-frequency (500–50 cm^{-1}) infrared spectra of Nujol mulls were recorded with a Digilab FTS-20B FT spectrophotometer.

Raman spectra of liquid Me_3CNC and of solid samples and solutions of the metal complexes held in sealed Pyrex capillary tubes were obtained at room temperature the 514.5 nm line from a Lexel 81 argon ion laser being used in conjuction with a Spex 1401 double monochromator. Polarization measurements were performed by consecutive scanning of peaks with the plane of the polarized light parallel and perpendicular, respectively, to the axis of an analyzer. The frequencies quoted are believed to be accurate to at least ± 2 cm^{-1}, apart from a few weak or broad peaks.

Results and discussion

A. t-Butyl isocyanide.

The vibrational spectrum of the free isocyanide will be discussed on the assumption that the molecule is a symmetric top [9] belonging to the C_{3v} point group, the vibrational spectra of other t-butyl compounds having been rationalized satisfactorily in this manner [3–8]. The fundamental vibrations will, therefore, be distributed as $9A_1 + 13E$, all infrared- and Raman-active (A_1 polarized, E depolarized), the remaining 4 A_2 fundamentals being infrared- and Raman-inactive. The 22 active fundamentals can be divided approximately into 5 methyl C–H stretches, 5 methyl deformations, 3 methyl rocking modes, and 1 methyl torsional mode, together with 8 skeletal modes. The methyl torsion (ν_{25}, E) has rarely, if ever, been observed directly in the vibrational spectra of t-butyl compounds and no band could be

Table 1

Infrared and Raman bands of liquid t-butyl isocyanide

Infrared (cm^{-1})	Raman (cm^{-1})	Assignment
3110 vw		$\nu_1 + \nu_{26}$
2992 vs	2991 ms (dp)	$\nu_{14}, \nu_{15}\ E\ \nu(CH_3)_{asym}$
	2957 ms (p)	$2\times\nu_4$
2946 m,br		$\nu_{16}E\ \nu(CH_3)_{sym}$
	2937 s (p)	$\nu_1A_1\ \nu(CH_3)_{asym}$
2920 sh	2919 s (p)	$\nu_2A_1\ \nu(CH_3)_{sym}$
2895 mw	2889 w	$2\times\nu_{18}$
2880 sh	2870 w	$\nu_{17} + \nu_{19}$
	2791 w	
	2729 w	$\nu_4 + \nu_6$
2305 w		$\nu_5 + \nu_{22}$
2137 vs	2135 vs (p)	$\nu_3A_1\ \nu(N{\equiv}C)$
2105 vw		$\nu_6 + \nu_7$
2068 vw		$\nu_7 + \nu_{20}$
1479 ms	1476 vw (p)	$\nu_4A_1\ \delta(CH_3)_{asym}$
1467 m		$\nu_{17}E\ \delta(CH_3)_{asym}$
1453 sh	1449 mw (dp)	$\nu_{18}E\ \delta(CH_3)_{asym}$
1402 w		$\nu_{19}E\ \delta(CH_3)_{sym}$
1373 s		$\nu_5A_1\ \delta(CH_3)_{sym}$
1238 s	1235 mw (p?)	$\nu_6A_1\ \nu(C-N)$
1217 s	1214 w	$\nu_{20}E\ \nu(CC_3)_{asym}$
1041 vw	1036 vw	$\nu_{21}E\ \rho(CH_3)$
930 vw	930 mw (dp?)	$\nu_{22}E\ \rho(CH_3)$
860 m	859 m (p)	$\nu_7A_1\ \rho(CH_3)$
	776 vw	$2\times\nu_9$
682 mw	684 m (p)	$\nu_8A_1\nu(CC_3)_{sym}$
514 w		$\nu_{23}E\ \rho(CC_3)$
398 w	394 w (p)	$\nu_9A_1\ \delta(CC_3)$
360 w	360 w (dp)	$\nu_{24}E\ \delta(CC_3)$
	181 s (dp)	$\nu_{26}E\ \delta(CNC)$

assigned to this vibration for the isocyanide. Table 1 lists the band frequencies of the liquid isocyanide together with proposed assignments. However, in a number of cases the descriptions of the assignments must be regarded as approximate as a result of mixing of modes, particularly those involving C–N or C–C_3 stretching and CH_3 rocking motions.

Methyl stretching modes. Assignments for these modes are not unambiguous because of overlapping and coincident bands and the possible presence of bending overtones. Five infrared- and Raman-active bands, ($2A_1 + 3E$), two of which should be polarized in the Raman effect, are predicted. However, apart from some weak features below 2900 cm^{-1}, which are ascribed to overtones or combinations, only four strong Raman bands are detected, but three are polarized. The infrared spectrum consists of one very strong band, one broad medium intensity band and a shoulder. The highest frequency Raman band, which is coincident with the very strong infrared band at 2992 cm^{-1}, is the only depolarized band in this region and so must be attributed to an E mode. In fact, we suggest that both CH_3 asymmetric stretches of E symmetry (ν_{14}, ν_{15}) are encompassed within the band envelope, in line with a similar assignment for t-butyl cyanide [7,8]. The lack of a further depolarized band in the Raman spectrum precludes assignment of the remaining E mode, ν_{16}, but it may contribute to the broad infrared band centered at 2946 cm^{-1}. Of the three polarized Raman bands, the two of greater intensity are assigned to the A_1 asymmetric and symmetric stretches, ν_1 and ν_2, respectively. Both have infrared counterparts, although it has to be suggested that the broad band at 2946 cm^{-1} contains overlapping ν_1 and ν_{16}. The highest frequency polarized Raman band is then assigned to an overtone of an A_1 CH_3 deformation. Assignments of analogous modes of the t-butyl halides are also bedeviled by accidental coincidences. For example, the infrared spectrum of the fluoride [3] has been assigned on the assumption that both A_1 modes and all three E modes are coincident, whereas Evans and Lo [4] with the advantage of Raman data have assigned the CH_3 stretching modes of the chloride quite differently, proposing that $\nu_1(A_1)$ is coincident with $\nu_{14}(E)$ and $\nu_2(A_1)$ coincident with $\nu_{15}(E)$. Kumar [8] has suggested that ν_1, ν_{14} and ν_{15} are all coincident (2980 cm^{-1}) in the infrared and Raman spectra of liquid t-butyl cyanide with $\nu_{16}(E)$ and $\nu_2(A_1)$ being assigned to bands at 2933 and 2912 cm^{-1}. However, the assignment of ν_{16} must be questionable because the band is apparently polarized in the Raman effect. Clearly, the problem of assigning CH_3 stretching modes in t-butyl compounds has not yet been resolved satisfactorily, although at least for the isocyanide our proposals are fully consistent with the polarization data.

Methyl deformation and rocking modes. Five methyl deformations ($2A_1 + 3E$) are predicted and, indeed, found in the infrared spectrum. However, only two bands, one being polarized, are apparent in the Raman spectrum. A similar situation is observed for t-butyl cyanide [7,8]. The assignments proposed here follow those of Crowder [7] for the cyanide but in view of the incomplete Raman data, reversal of the assignments of ν_5 and ν_{19} as suggested by Kumar [8] cannot be ruled out. However, whereas for the cyanide Crowder [7] suggests accidental degeneracy of ν_4 and ν_{17} and Kumar [8] proposes a similar situation for ν_{17} and ν_{18}, no such assumptions are required in our proposed assignments for the isocyanide.

For the methyl rocking modes ($A_1 + A_2 + 2E$), three bands are predicted and observed in both the infrared and Raman spectra. The polarized band must be assigned to the A_1 fundamental ν_7 and the assignments are in overall agreement with those of t-butyl cyanide [7,8] and acetylide [6].

Skeletal stretching modes. These are distributed as $3A_1 + E$, approximate descriptions being $\nu(N{\equiv}C)$, A_1, $\nu(CN)$, A_1, which is likely to be strongly coupled with $\rho_{sym}(CH_3)$, and two $\nu(CC_3)$ modes, $A_1 + E$, the latter being coupled with $\rho(CH_3)$ and $\delta(CH_3)$ E modes [7]. The very strong infrared and highly polarized Raman bands at 2137 cm^{-1} are obviously assigned to $\nu(N{\equiv}C)$, ν_3. The symmetric $\nu(CC_3)$ stretch, ν_8, is assigned to the infrared and polarized Raman bands at 684 cm^{-1}. This agrees well with similar assignments for other Me_3CX species (i.e. $X = CN$, 695 cm^{-1}; $X = C{\equiv}CH$, 690 cm^{-1}) except when $X =$ halide for which ν_8 falls in the range 750–820 cm^{-1}. This leaves the other $\nu(CC_3)$ fundamental, ν_{20}, and the $\nu(CN)$ stretch, ν_6. Two bands are found in the 1200–1250 cm^{-1} region of both the infrared and Raman spectra of the isocyanide. The higher frequency band (1235 cm^{-1}) is strong in the infrared but only of medium-weak intensity in the Raman spectrum; it is assigned to the A_1 fundamental ν_6 on the basis of polarization data. The lower frequency band at 1214 cm^{-1}, which is also strong in the infrared but weak in the Raman spectrum, is assigned to the E fundamental, ν_{20}.

Skeletal bending modes. The four skeletal bending modes are $\rho(CC_3)$, E, $\delta(CN{\equiv}C)$, E, $\delta_{sym}(CC_3)$, A_1 and $\delta_{asym}(CC_3)$, E. By analogy with assignments for other Me_3CX species at least three of these should be found below 400 cm^{-1}. For the cyanide Crowder [7] suggests that a very weak band at 578 cm^{-1} should be assigned to $\rho(CC_3)$, ν_{23}. However, Kumar [8] proposed the assignment $3 \times \nu_{26}$ for this band, the ν_{23} fundamental supposedly being coincident with ν_{24}, the $\delta_{asym}(CC_3)$ mode. The infrared spectrum of liquid t-butyl isocyanide has a weak band at 514 cm^{-1} which has no counterpart in the Raman spectrum. We assign this band to ν_{23} since normal coordinate calculations indicate that this fundamental is very sensitive to the nature of X in Me_3CX (e.g. it is expected to be near 537 cm^{-1} for $X = C{\equiv}N$ [7], 460 cm^{-1} for $X = F$ and as low as 386 cm^{-1} for $X = I$ [4]. The only polarized Raman band below 400 cm^{-1} is found at 394 cm^{-1} and is assigned to ν_9, $\delta_{sym}(CC_3)$; it has a weak infrared counterpart at 398 cm^{-1}. The depolarized Raman band and its weak infrared partner at 360 cm^{-1} is assigned to ν_{24}, $\delta_{asym}(CC_3)$. The analogous ν_9 and ν_{24} fundamentals of the cyanide appear at 384 and 369 cm^{-1}, respectively [7]. The one remaining depolarized Raman band of strong intensity at 181 cm^{-1} must therefore be assigned to ν_{26}, $\delta(CN{\equiv}C)$. It was not observed in the infrared spectrum because our study terminated at 200 cm^{-1}. The $\delta(CC{\equiv}N)$ fundamental is observed as a strong Raman band at 198 cm^{-1} for the cyanide [7,8].

B. The hexakis(t-butyl isocyanide) metal complexes

No structural determinations have been reported for the three complexes studied in this work, so as a first approximation the $M(CNC)_6$ skeletons will be treated as possessing local octahedral symmetry. We and others have adopted this approach previously in an analysis of the vibrational spectra of other $[M(CNR)_6]^{n+}$ (M = Re, $n = 1$ [10], M = Mn, $n = 1, 2$ [11]) cations. Although a few metal isocyanide complexes are known [15] with CNC angles considerably less than 180°, this is most unlikely for the cations studied here. Indeed, crystallographic studies of related t-butyl isocyanide metal complexes, for example, octahedral $[V(CNCMe_3)_6]^{2+}$ [16], and distorted capped trigonal prismatic $[Mo(CNCMe_3)_7]^{2+}$ [17], show that all MCN angles are greater than 174° and all CNC angles greater than 177°. Therefore, we feel justified in employing O_h symmetry arguments as a basis for assigning the vibrational bands. Of course, the entire cations cannot possess strict O_h symmetry because inclusion of the t-butyl groups restricts the highest achievable symmetry to S_6. The attainment of S_6 symmetry would minimize steric interactions between t-butyl groups. Band splittings thought to result from lowering of the symmetry from O_h will be mentioned as appropriate. Proposed assignments of the solid state infrared and Raman spectra of the three complexes are listed in Tables 2 and 3, together with approximate descriptions of the normal modes. The results of a dichloromethane solution study in the $\nu(N{\equiv}C)$ region are given in Table 4, together with Raman polarization data.

The assignments of infrared ($2\ T_{1u}$) and Raman ($A_{1g} + E_g + T_{2g}$) bands to PF_6^- fundamentals are straightforward (Table 2). The E_g $\nu(PF)$ asymmetric stretch has not been observed for the rhenium complex and the $2T_{1u} + T_{2g}$ deformations are usually found as bands displaying well-resolved splitting.

The $\nu(N{\equiv}C)$ bands (Tables 2 and 4) are the most intense bands in both the infrared and Raman spectra of the three complexes and as a result of polarization measurements on dichloromethane solutions present no problems for assignment.

Table 2

Vibrational spectra (cm^{-1}) of solid [M(CNCMe$_3$)$_6$](PF$_6$)$_n$

Description		Activity	M = Re, $n = 1$		M = Ru, $n = 2$		M = Os, $n = 2$	
			IR	Raman	IR	Raman	IR	Raman
PF$_6^-$ Fundamentals (O_h)								
ν Sym. stretch	A_{1g}	R		744 s		741 vs		747 s 739 s
ν_2 Asym. stretch	E_g	R		–		564 vw		561 w,br
ν_3 Deformation	T_{1u}	IR	847 sh 843 vs		842 vs		844 vs	
ν_4 Deformation	T_{1u}	IR	568 sh 563 s		565 vs 545 sh		559 s 547 sh	
ν_5 Deformation	T_{2g}	R		469 sh 458 m		475 sh 452 m		476 sh 464 m
M(CNC)$_6$ Fundamentals (O_h)								
ν(N≡C)	A_{1g}	R		2184 s		2252 s		2256 vs
ν(N≡C)	E_g	R		2101 vs 2063 sh		2208 vs		2208 sh 2203 vs
ν(N≡C)	T_{1u}	IR	2096 vs 2056 vs		2197 vs		2192 vs	
ν(MC)	A_{1g}	R		298 w		282 w		292 w
ν(MC)	E_g	R		235 w		236 w		237 w
ν(MC)	T_{1u}	IR	227 m		239 m		235 sh 220 m	
δ(MCN)	T_{2g}	R		503 w		528 w		528 w
δ(MCN)	T_{1u}	IR	467 w		474 m		467 w	

Table 3

t-Butyl bands (cm^{-1}) in the vibrational spectra of solid [M(CNCMe$_3$)$_6$](PF$_6$)$_n$

Description	M = Re, $n = 1$		M = Ru, $n = 2$		M = Os, $n = 2$	
	IR	Raman	IR	Raman	IR	Raman
ν(CH$_3$)	2978 m	2993 m	2988 sh	2994 ms	2985 mw	2993 m
	2938 w	2946 mw	2982 mw	2965 sh	2946 w	2960 sh
	~ 2930 sh	2925 m	2943 w	2935 ms	~ 2930 sh	2934 m
						2912 sh
Overtones and combinations	2876 vw	2870 vw	2882 vw	2874 w	2890 vw	2874 vw
		2784 vw	~ 2860 sh	2798 w	~ 2860 sh	
				2733 w		
δ(CH$_3$)	1458 mw	1470 mw	1476 sh	1477 sh	1476 sh	~ 1470 sh
	1442 vw,sh	1458 mw	1460 mw	1459 ms	1458 w	1459 s
	1407 vw,sh	1413 vw	1403 mw	1403 mw	1403 w	
	1396 vw	1396 vw	1372 m		1372 m	
	1369 ms					
	1365 sh					
ν(CN)	1233 m	1231 m	1238 m	1237 ms	1238 m	1237 ms
		1210 m	1210 sh	1209 w	1210 sh	1204 w,br
ν(CC$_3$)$_{\text{asym}}$	1205 s		1188 ms		1191 ms	
ρ(CH$_3$)	1041 vw	1039 w	936 w	1043 mw	938 vw	1045 mw
	928 vw	926 m	874 w	935 m	877 w	933 ms
	876 mw	880 ms		856 m		880 sh
						856 ms
δ(CC$_3$)	436 m,br	374 vw	436 m	420 w	446 mw	367 vw
	350 vw	350 vw	357 w	360 vw	357 w	340 w
				344 mw		
δ(CNC)		213 m				

Table 4

ν(N≡C) bands ($\mathrm{cm^{-1}}$) and force constants (10^2 N $\mathrm{m^{-1}}$) from dichloromethane solution spectra

Complex	A_{1g} Raman	E_g Raman	T_{1u} IR	k(NC)	k_i(NC)
$[\mathrm{Re(CNCMe_3)_6}]\mathrm{PF_6}$	2182 (p)	2103 (dp)	2098 2058	16.84	0.21
$[\mathrm{Ru(CNCMe_3)_6}](\mathrm{PF_6})_2$	2250 (p)	2211 (dp)	2199	18.61	0.11
$[\mathrm{Os(CNCMe_3)_6}](\mathrm{PF_6})_2$	2250 (p)	2207 (dp)	2200	18.54	0.12

These polarization results show that the highest frequency Raman band is the A_{1g} mode and the lower the E_g mode. The infrared-active T_{1u} fundamental appears at a slightly lower frequency (5–12 $\mathrm{cm^{-1}}$) than the Raman-active E_g mode for all three complexes. The T_{1u} band of $[\mathrm{Re(CNCMe_3)_6}]\mathrm{PF_6}$ is markedly split in both the solid state and dichloromethane solution infrared spectra into two components of almost equal intensity separated by 40 $\mathrm{cm^{-1}}$, but no such splitting is observed for the ruthenium and osmium complexes which therefore follow an O_h approach. Should S_6 symmetry be appropriate for the rhenium complex, this would be the expected result, the Raman-active A_{1g} and E_g modes now transforming as Raman-active A_g and E_g, respectively, whereas the infrared-active T_{1u} mode transforms as $A_u + E_u$, both components being infrared-active only. However, in the solid state spectra of the rhenium and osmium complexes, but not in the solution spectra, the Raman-active E_g bands also show discernable shoulders with a separation from the major component of 38 and 5 $\mathrm{cm^{-1}}$, respectively. The large separation for the rhenium compound may be indicative of a lowering of the true symmetry below S_6. Additional extremely weak, broad, shoulders are observed in the solid state infrared spectra of all three compounds some 150 $\mathrm{cm^{-1}}$ below the T_{1u} bands (Re, 1940; Ru, 2045; Os, 2042 $\mathrm{cm^{-1}}$). A similar feature has been noted previously [10] for $[\mathrm{Re(CNMe)_6}]\mathrm{PF_6}$. The origin of these very weak shoulders is not clear but it has been suggested that deviation from strict linearity of the MC≡NC groups may be responsible.

We have reported previously [10] that the Raman-active A_{1g} ν(N≡C) bands are considerably less intense than the E_g ν(N≡C) bands for $[\mathrm{Re(CNR)_6}]^+$, (R = Me, Ph, or *p*-tol). This anomalous effect has also been observed for the ν(C≡O) bands of low spin d^6 metal hexacarbonyls $\mathrm{M(CO)_6}$ (M = Cr, Mo, or W) and $[\mathrm{Re(CO)_6}]^+$ [18]. The same feature has been found for the low spin d^6 metal hexakis(isocyanide) complexes considered here and is more pronounced for the rhenium(I) cation than for the ruthenium(II) and osmium(II) cations. Using peak area measurements from the solid state Raman spectra, the $I_\nu(A_{1g})/I_\nu(E_g)$ ratios are approximately 0.15, 0.35 and 0.30 for rhenium, ruthenium and osmium, respectively. The intensity ratio, therefore, decreases as the formal oxidation state of the metal is lowered. This effect has been observed [11] for a range of $[\mathrm{Mn(CNR)_6}]^{n+}$ cations where for $n = 1$ the E_g band is more intense than the A_{1g} band whereas for $n = 2$ the two bands are of approximately equal intensity. These anomalous intensity ratios have been related to polarizability changes of opposite sign along and perpendicular to the C–O bond axis for the metal carbonyls. As organic isocyanides bond to transition metals in a similar synergic manner to carbon monoxide, a related explanation may be appropriate.

Taking into consideration the σ-donor and π-acceptor abilities of t-butyl isocyanide with respect to the three low spin d^6 metals, it would be expected that back-donation from ruthenium(II) and osmium(II) should be less than that from rhenium(I) because of the greater positive charge residing on the former two metal centers. Accordingly, the NC bond order should be greater in the ruthenium(II) and osmium(II) complexes than in the rhenium(I) complex. The results listed in Tables 2 and 4 show that the frequencies of the A_{1g}, E_g and T_{1u} bands are found at higher wavenumbers for the ruthenium(II) and osmium(II) complexes (ca. 2260–2190 cm^{-1}) than for the rhenium(I) complex (2184–2056 cm^{-1}). Nielson and Wherland [11] calculated NC force constants for the $[Mn(CNR)_6]^{n+}$ ($n = 1, 2$) cations using the Cotton–Kraihanzel approach [19] developed for metal carbonyls. We have, therefore, also carried out these calculations using the solution data listed in Table 4. The resulting NC force constants, k(NC), and stretch-stretch interaction constants, k_i(NC) are also listed in Table 4 and may be compared with the NC force constant of free t-butyl isocyanide, 17.38×10^2 Nm^{-1}, calculated using the expression [20] $k = 0.5889\ \nu^2 m$, where $\nu = 2137$ cm^{-1} and $m = 6.464$, the reduced mass of the NC group.

The utility of this approach has been assessed by calculating k(NC) from $\lambda E_g = \mu k(\mathrm{NC})$, then obtaining k_i(NC) from $\lambda A_{1g} = \mu(k(\mathrm{NC}) + 6\ k_i(\mathrm{NC}))$ and finally using the results to calculate an estimated value for the T_{1u} ν(NC) frequency from $\lambda T_{1u} = \mu(k(\mathrm{NC}) - 2k_i(\mathrm{NC}))$. The estimated T_{1u} ν(NC) frequencies were found to be in excellent agreement with the values obtained directly from infrared spectra.

In accord with expectations, the NC force constants for the ruthenium(II) and osmium(II) cations are in close agreement, both being considerably greater than k(NC) for the rhenium(I) cation. The interaction constant k_i(NC) is much greater for rhenium(I) than for the other two cations. The NC force constant of free t-butyl isocyanide falls between those of the rhenium(I) cation and the ruthenium(II), osmium(II) pair, but is closer to that of the rhenium species. The differences [k(NC) free ligand − k(NC) complex] are 0.54, − 1.23 and − 1.16×10^2 Nm^{-1} for rhenium, ruthenium and osmium, respectively. This clearly demonstrates that significant metal-to-ligand π-back-donation occurs for rhenium(I) but is absent or greatly reduced for the metal(II) complexes. The increase in k(NC) for the metal(II) cations relative to that of the free ligand has been attributed to increased electron donation from the isocyanide lone-pair orbital which will, in turn, increase the CN bond strength by removal of the slightly negative overlap population between carbon and nitrogen in the isocyano group. This negative overlap population has been indicated in ab initio MO calculations on isocyanides [11].

Proposed assignments for δ(MCN) and ν(MC) modes are also listed in Table 2. By analogy with other metal isocyanide complexes, bands of higher frequency are assigned to δ(MCN). The bands in both the Raman and infrared spectra are, at best, of very moderate intensity and most are weak, so assignments must be regarded as tentative in the absence of polarization data. A further complication is the presence of bands associated with t-butyl δ(CC_3) deformations. In line with the selection rules for O_h symmetry, one Raman-active (T_{2g}) and one infrared-active (T_{1u}) band has been assigned to δ(MCN) in the 460–530 cm^{-1} region. The remaining two δ(MCN) modes ($T_{1g} + T_{2u}$) are inactive. Two Raman-active bands ($A_{1g} + E_g$) and one infrared-active band (T_{1u}) in the 220–300 cm^{-1} region have been assigned to ν(MC) stretches. This range is similar to that suggested for ν(ReC) bands of other $[Re(CNR)_6]^+$ cations (R = Me, Ph, or *p*-tol) [10], but not to that (405 cm^{-1}) proposed [12] for $\nu_{sym}(ReC)$ of $[Re_2(CO)_{10-n}(CNCMe_3)_n]$ species ($n = 1$–3). Conversely, bands as low as 196 cm^{-1} ($n = 1$) and 170 cm^{-1} ($n = 2$) have been assigned [11] to A_{1g} $\nu(MnC)$ modes of $[Mn(CNCMe_3)_6]^{n+}$.

The remaining infrared and Raman bands observed for the three cations are listed in Table 3 and assigned to internal t-butyl group vibrations by comparison with the free ligand band assignments fully discussed earlier. More detailed assignments would not be justified.

Acknowledgement

Support from the National Science Foundation (Grant No. CHE85-06702) is gratefully acknowledged.

References

1 L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley-Interscience, New York, 1969.
2 R.G. Snyder and J.H. Schachtschneider, Spectrochim. Acta, 21 (1965) 169.
3 D.E. Mann, N. Acquista and D.R. Lide, J. Mol. Spectrosc., 2 (1958) 575.
4 W. Huttner and W. Zeil, Spectrochim. Acta, 22 (1966) 1007.
5 J.C. Evans and G.Y.-S. Lo, J. Am. Chem. Soc., 88 (1966) 2118.
6 N. Sheppard, J. Chem. Phys., 17 (1949) 455.
7 G.A. Crowder, J. Phys. Chem., 75 (1971) 2806.
8 K. Kumar, Spectrochim. Acta A, 28 (1972) 459.
9 B. Bak, L. Hansen-Nygaard and J. Rastrup-Andersen, J. Mol. Spectrosc., 2 (1958) 54.
10 C. Cameron, R.A. Walton and D.A. Edwards, J. Organomet. Chem., 262 (1984) 335.
11 R.M. Nielson and S. Wherland, Inorg. Chem., 24 (1985) 1803.
12 P.D. Harvey, I.S. Butler, G.W. Harris and N.J. Coville, Inorg. Chem., 25 (1986) 3608.
13 J.D. Allison, T.E. Wood, R.E. Wild and R.A. Walton, Inorg. Chem., 21 (1982) 3540.
14 S.M. Tetrick and R.A. Walton, Inorg. Chem., 24 (1985) 3363.
15 E. Singleton and H.E. Oosthuizen, Adv. Organomet. Chem., 22 (1983) 209.
16 L.D. Silverman, P.W.R. Corfield and S.J. Lippard, Inorg. Chem., 20 (1981) 3106.
17 D.L. Lewis and S.J. Lippard, J. Am. Chem. Soc., 97 (1975) 2697.
18 S.F.A. Kettle, I. Paul and P.J. Stamper, J. Chem. Soc. Dalton Trans., (1972) 2413; M.R. Afiz, R.J.H. Clark and N.R. D'Urso, ibid., (1977) 250; E.W. Abel, R.A.N. McLean, S.P. Tyfield, P.S. Braterman, A.P. Walker and P.J. Hendra, J. Mol. Spectrosc., 30 (1969) 29.
19 F.A. Cotton and C.S. Kraihanzel, J. Am. Chem. Soc., 84 (1962) 4432.
20 T.T.T. Li, M.J. Weaver and C.H. Brubaker, J. Am. Chem. Soc., 104 (1982) 2381.