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VIBRATIONAL SPECTRA OF THORACENE AND THE POTASSIUM SALT OF DICYCLOOCTATETRAENYLLANTHANUM

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Summary

The vibrational spectra of crystalline thoracene and the potassium salt of dicyclooctatetraenyllanthanum have been recorded, and assignments of the ligand frequencies made by comparison with the spectra of potassium cyclooctatetraenide. All the vibrational frequencies of the cyclooctatetraenyl dianion were found to rise on coordination to a metal. Analysis of the spectra in the range of the ligand and skeletal modes suggests stronger coordination bonds in the thorium complex compared to that of lanthanum.

Introduction

The chemistry of cyclooctatetraenyl complexes of transition metals is a comparatively new area of organometallic chemistry. These compounds have aroused great interest since uranocene, the first homo-ligand sandwich complex containing cyclooctatetraenyl ligands (Cot), was obtained and its properties studied [1]. In uranocene, both planar 8-membered cycles are bound to the uranium atom, so that the complex has an overall D_{8h} symmetry with an eclipsed ligand conformation [2]. Compounds of similar structure have likewise been obtained for thorium [2] and other actinides (An) [3]. Sandwich complexes with Cot ligands are also known for lanthanides (Ln) [4,5]. However, no sandwich compounds containing Cot ligands have been obtained as yet for the *d*-transition metals. Investigation of the physical and chemical properties of Cot_2An complexes has shown that they represent a novel class of metallocenes with a covalent type of coordination [6,7]. The covalent bond is realized by overlap of the metal $5f_{\pm 2}$ orbitals with the e_{2u} orbitals of the ligands [6,7]. Recent investigation of photoelectron spectra of uranocene and thoracene [8]

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have shown that overlap of metal $6d_{\pm 2}$ orbitals with the ligand e_{2g} orbitals makes a substantial contribution to the bonding scheme. Analysis of chemical and magnetic measurement data for Cot complexes of lanthanides suggests that the covalent component of the bonding in these complexes is small, which is due to the weakness of the interaction of the metal 4*f* orbitals with the corresponding ligand orbitals, arising from energetic reasons [9]. It is assumed [10] that, unlike the An complexes, the coordination bond in the Ln complex possesses considerably more ionic character.

This paper is devoted to a comparatively study of the vibrational spectra of Cot complexes with actinide and lanthanide metals, as exemplified by thoracene and the potassium salt of dicyclooctatetraenyllanthanum; the following problems are discussed:

a) The assignments of fundamental vibrational frequencies of the complexes;

b) The changes in the vibrational frequencies of the ligands due to their coordination with the metal, comparing them for complexes of both series of *f*-transition metals.

For the complexes $K(LaCot_2)$, IR data have been reported in the range 600—1200 cm^{-1} only [9,10]. Complete IR and Raman spectra are reported for $ThCot_2$ in ref. 11. An attempt to analyse the IR spectra of Cot complexes has been made in ref. 12.

Experimental

Thoracene was prepared according to a known method [13] and purified by repeated sublimation at 1×10^{-4} Torr. The lanthanum complex was prepared according to reported procedures [9]. According to the report the complex was green and this would be a hinderance to obtaining its Raman spectrum. However, we succeeded in obtaining yellow samples using highly purified cyclooctatetraene and by thorough washing with THF. Accordingly, the green colour of the complex described was due to impurities.

The IR spectra in the 250—4000 cm^{-1} range were measured on UR-20 and Perkin-Elmer 457 spectrophotometers for Nujol and fluorolube mulls, avoiding contact of the sample with moisture and air; nevertheless, we observed several weak bands due to oxidation products in the IR spectra of the La complexes.

The Raman spectra were measured on samples sealed in thin capillaries with Coderg-PHO and Ramanor-HG2S spectrometers equipped with holographic gratings. The He/Ne and Ar^+ laser lines were used for excitations. The Raman spectra of $ThCot_2$ were recorded for the samples at room and at liquid nitrogen temperatures. At low temperature most of the Raman bands were observed to split into several components.

The spectral data are presented in Tables 1 and 2.

Results and discussion

Ligand modes

In assigning the ligand vibrations, we made use of the data on the analysis of vibrational spectra of the dianion $C_8H_8^{2-}$ [14,15]. In making the assignments we adhered to the following principles which are justified by the analysis of a

TABLE 1

VIBRATIONAL SPECTRA AND ASSIGNMENTS FOR $\mathrm{ThCot_2}$ [a]

Infrared ($\mathrm{cm^{-1}}$)	Raman ($\mathrm{cm^{-1}}$)		Assignment
	Room temp.	Low temp.	
		28w	
	68w	68w	Lattice vibrations
		81w	
	221 225 } vs	224 228 } vs	$\nu(\mathrm{ML})$, A_{1g}
	240vs	243 246 248 } vs	$\nu(\mathrm{ML})^{\mathrm{tilt}}$, E_{1g}
246s			$\nu(\mathrm{ML})$, A_{2u}
	264m	266 271 } m	$\chi(\mathrm{CCC})$, E_{2g}
375m [b]			($\nu(\mathrm{ML})$, E_{1u})
	388s	383 388 392 } s	$\gamma(\mathrm{CCC})$, E_{2g}
512vw			
699vs			$\rho(\mathrm{CH})$, A_{2u}
	720m	724m	$\rho(\mathrm{CH})$, A_{1g}
744s			$\nu(\mathrm{CC})$, A_{2u}
	740vs	754vs	$\nu(\mathrm{CC})$, A_{1g}
	767(sh)	772w	$\rho(\mathrm{CH})$, E_{1g}
777m			$\rho(\mathrm{CH})$, E_{1u}
790w	790vw	790vw	
823vw			
840vw	853vw	856vw	($\rho(\mathrm{CH})$, E_{2g})
900s			$\beta(\mathrm{CH})$, E_{1u}
	894w	896w	$\beta(\mathrm{CH})$, E_{1g}
978vw			
1022vw			
1088vw			($\gamma(\mathrm{CCC})$, B_{1g} or $\rho(\mathrm{CH})$, B_{2u})
1180vw	1180vw	1182vw	($\beta(\mathrm{CH})$, B_{2g})
	1308vw	1308vw	$\nu(\mathrm{CC})$, E_{1g}
1319m			$\nu(\mathrm{CC})$, E_{1u}
1430w	1430vw		(699 + 744 or $\nu(\mathrm{CC})$, E_{3g})
1470w			699 + 777?
1500w(br)	1497s	1497s	$\nu(\mathrm{CC})$, E_{2g}
1603w(br)			
1630w(br)			
1750m(br)			
1861m(br)			
2870vw	2852vw		
2922vw	2928vw	2931vw	
	2979vw	2977 2982 } w	$\nu(\mathrm{CH})$, E_{2g}
3020w	3018m	3015 3020 } w	$\nu(\mathrm{CH})$, E_{1u} and E_{1g}
3042w	3039s	3041 3046 } m	$\nu(\mathrm{CH})$, A_{1g} and A_{2u}

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[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

[b] This band observed in the spectrum was recorded by Goffard [11]. In the spectrum recorded by us there is a broad, weak band from the CsI windows in this region.

TABLE 2

VIBRATIONAL SPECTRA AND ASSIGNMENTS FOR $KLaCot_2$

Infrared (cm^{-1})	Raman (cm^{-1})	Assignment
	137w	Lattice mode?
	202vs	Skeletal modes, see text
	216vs	
	369s	ν(CCC), E_{2g}
575w(br)		
628w		Oxidate mode
680vs		ρ(CH), A_{2u}
740m		ν(CC), A_{2u}
	743vs	ν(CC), A_{1g}
771w		ρ(CH), E_{1u}
	840vw(br)	(ρ(CH), E_{2g})
892s		β(CH), E_{1u}
975vw		Oxidate mode
1034m(br)		
1091w		(ν(CCC), B_{1g} or ρ(CH), B_{2u})
1170vw		(β(CH), B_{2g})
1312m		ν(CC), E_{1u}
1453vw	1493m	ν(CC), E_{2g}
1582(br)m		
1732m(br)		
1832m(br)		
2862vw		
3011m	3010vw	ν(CH) E_{1u} and E_{1g}
3038w	3040w	ν(CH), A_{1g} and A_{2u}

series of Cp complexes of transition metals and complexes with other aromatic ligands [16].

a) The bands corresponding to the allowed vibrations of the $C_8H_8^{2-}$ dianion should manifest themselves strongly in the vibrational spectra of the Cot_2M complexes.

b) In the spectra of Cot_2M vibrational bands forbidden for the "free" dianion but allowed for the CotM model may appear; the stronger the M—Cot bond, the higher the intensities of these bands.

c) Interaction between similar modes of the two Cot rings via the metal atom should lead to pairs of vibrations, "gerade" and "ungerade" with respect to the inversion centre. Since this interaction is weak, the corresponding frequencies should have similar values. The correlations of the symmetry species of the $C_8H_8^{2-}$, C_8H_8M and $(C_8H_8)_2M$ models are given in Table 3.

Indeed, one can clearly see that the frequencies and relative intensities of some bands in the spectra of the complexes (Figs. 1 and 2) are fairly close to those in the spectrum of the salt $K_2C_8H_8$ [14,15]. These are the following six bands observed in the Raman spectra of thoracene (potassium salt of dicyclooctatetraënyllanthanum) at 388(369), 750(743), 767, 1497(1493), 3039(3039) and 2979 cm^{-1}, and which are related to the γ(CCC)(E_{2g}), ν(CC)(A_{1g}), ρ(CH)(E_{1g}), ν(CC)(E_{2g}), ν(CH)(A_{1g}) and ν(CH)(E_{2g}) modes, respectively. The IR spectrum reveals four prominent bands at 699(680), 900(892), 1319(1312) and 3017(3011) cm^{-1} related to the ρ(CH)(A_{2u}), β(CH)(E_{1u}), ν(CC)(E_{1u}) and ν(CH)(E_{1u}) modes, respectively. The eleventh mode, β(CH)(E_{2g}), allowed in the

TABLE 3

CORRELATION TABLE FOR VIBRATIONS OF Cot, CotM AND Cot_2M [a]

Vibration	Cot dianion (D_{8h})		CotM (C_{8v})		Cot$_2$M (D_{8h})			
	symm.	selection rules	symm.	selection rules	symm.	selection rules	symm.	selection rules
ν(CH)	A_{1g}	R	A_1	R, IR	A_{1g}	R	A_{2u}	IR
ν(CC)	A_{1g}	R	A_1	R, IR	A_{1g}	R	A_{2u}	IR
ρ(CH)	A_{2u}	IR	A_1	R, IR	A_{1g}	R	A_{2u}	IR
β(CH)	A_{2g}	n.a.	A_2	n.a.	A_{2g}	n.a.	A_{1u}	n.a.
ν(CC)	B_{1g}	n.a.	B_1	n.a.	B_{1g}	n.a.	B_{2u}	n.a.
β(CH)	B_{1g}	n.a.	B_1	n.a.	B_{1g}	n.a.	B_{2u}	n.a.
ρ(CH)	B_{1u}	n.a.	B_2	n.a.	B_{2g}	n.a.	B_{1u}	n.a.
χ(CCC)	B_{1u}	n.a.	B_2	n.a.	B_{2g}	n.a.	B_{1u}	n.a.
ν(CH)	B_{2g}	n.a.	B_2	n.a.	B_{2g}	na	B_{1u}	n.a.
γ(CCC)	B_{2g}	n.a.	B_2	n.a.	B_{2g}	n.a.	B_{1u}	n.a.
ρ(CH)	E_{1g}	R	E_1	R, IR	E_{1g}	R	E_{1u}	IR
ν(CH)	E_{1u}	IR	E_1	R, IR	E_{1g}	R	E_{1u}	IR
ν(CC)	E_{1u}	IR	E_1	R, IR	E_{1g}	R	E_{1u}	IR
β(CH)	E_{1u}	IR	E_1	R, IR	E_{1g}	R	E_{1u}	IR
ν(CH)	E_{2g}	R	E_2	R	E_{2g}	R	E_{2u}	n.a.
ν(CC)	E_{2g}	R	E_2	R	E_{2g}	R	E_{2u}	n.a.
β(CH)	E_{2g}	R	E_2	R	E_{2g}	R	E_{2u}	n.a.
γ(CCC)	E_{2g}	R	E_2	R	E_{2g}	R	E_{2u}	n.a.
ρ(CH)	E_{2u}	n.a.	E_2	R	E_{2g}	R	E_{2u}	n.a.
χ(CCC)	E_{2u}	n.a.	E_2	R	E_{2g}	R	E_{2u}	n.a.
ρ(CH)	E_{3g}	n.a.	E_3	n.a.	E_{3g}	n.a.	E_{3u}	n.a.
χ(CCC)	E_{3g}	n.a.	E_3	n.a.	E_{3g}	n.a.	E_{3u}	n.a.
ν(CH)	E_{3u}	n.a.	E_3	n.a.	E_{3g}	n.a.	E_{3u}	n.a.
ν(CC)	E_{3u}	n.a.	E_3	n.a.	E_{3g}	n.a.	E_{3u}	n.a.
β(CH)	E_{3u}	n.a.	E_3	n.a.	E_{3g}	n.a.	E_{3u}	n.a.
γ(CCC)	E_{3u}	n.a.	E_3	n.a.	E_{3g}	n.a.	E_{3u}	n.a.

[a] Abbreviations: R, allowed vibration in Raman spectrum; IR, allowed vibration in infrared spectrum; n.a., inactive vibration.

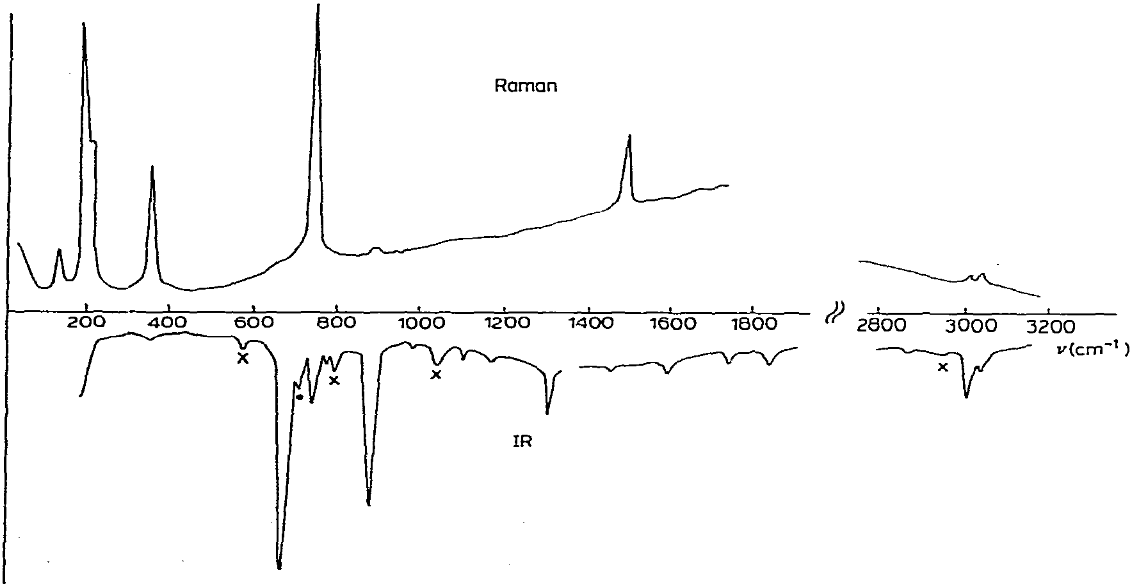

Fig. 1. Infrared and Raman spectra of $KLaCot_2$. IR spectrum in the 250—1350 cm^{-1} region is recorded for $KLaCot_2$ in Nujol and in the 1350—3200 cm^{-1} region in a fluorolube mull. ○ band of Nujol, X Bands of decomposition product, these bands are strong in the spectrum of the brown colour oxidate.

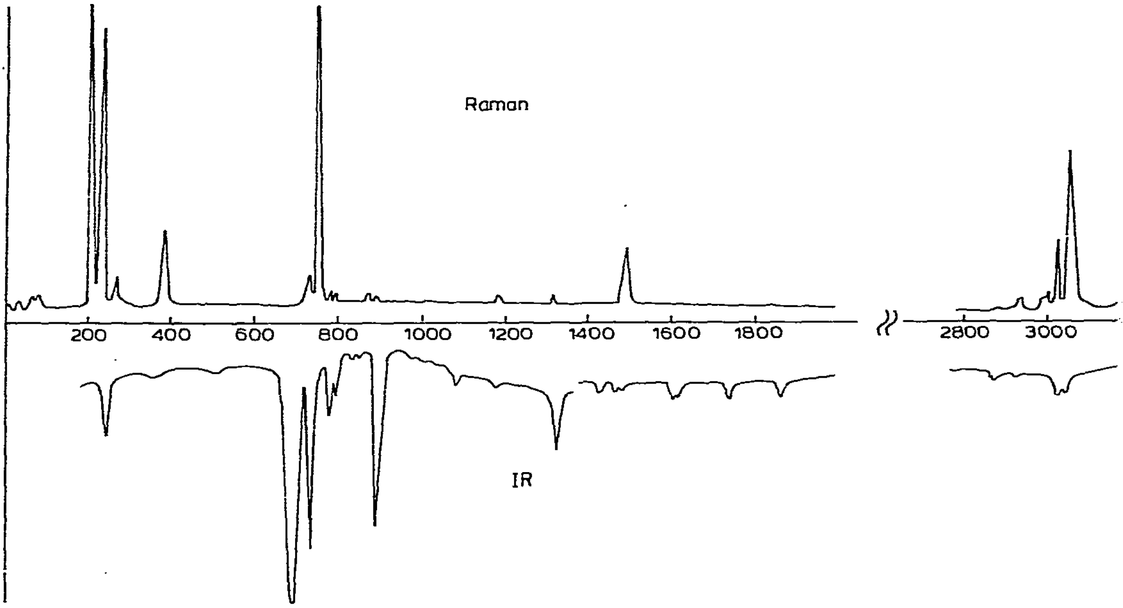

Fig. 2. Infrared and Raman spectra of $ThCot_2$.

Raman spectrum of the dianion, was not found in the Raman spectrum of the complexes. According to reported data [14] the frequency of this mode appear in the range 900—1100 cm^{-1}; however, no bands of appreciable intensity are seen in this range.

When the local symmetry of the ligand in the complex is decreased to C_{8v}, bands are expected to appear in the IR spectra of the complexes corresponding to the ungerade analogs of $\nu(CC)(A_{1g})$, $\rho(CH)(E_{1g})$, $\nu(CH)(A_{1g})$ modes of the dianion which are allowed in the Raman spectrum (Table 3). These are the bands found in the spectrum of thoracene (potassium salt of dicyclooctatetraenyllanthanum) at 744(740), 777(771) and 3042(3038) cm^{-1}; their relative intensity being higher in the spectrum of $ThCot_2$, as compared to that of $KLaCot_2$ (cf. Figs. 1 and 2). Weak bands at 894 and 1308 cm^{-1}, and two medium bands at 720 and 3018 cm^{-1} are the gerade analogs of four modes allowed in the IR spectrum of dianion $C_8H_8^{2-}$. Two modes, $\chi(CCC)(E_{2g})$ and $\rho(CH)(E_{2g})$, which have no analogs in the spectrum of the dianion (Table 3), are also allowed in the Raman spectra of the complexes. Since the frequencies of the out-of-plane $\chi(CCC)(E_{2g})$ bending modes should lie lower than that of in-plane $\gamma(CCC)(E_{2g})$, we can assign the moderately strong band at 264 cm^{-1} to the $\chi(CCC)(E_{2g})$ mode. The weak Raman band at 853 cm^{-1} can be assigned to the $\rho(CH)(E_{2g})$ mode.

A variety of weak bands was observed, possibly due either to transition to higher orders or to violation of the selection rules in the crystalline phases. Thus, the low local symmetry of the thoracene molecules in the lattice cell of the crystal (C_1, according to X-ray structure data [2]) allows the appearance of all the gerade modes of the complex in the Raman spectrum and the ungerade modes in the IR spectrum. (No data on the crystalline structure of the La complex are available.) The assignments of these weak bands are tentative and are presented in parentheses in Tables 1 and 2.

The frequencies of all the vibrational modes of the ligand are increased on coordination (Table 4). The highest shift is observed for the in-plane CCC bending mode (up to 40 cm^{-1}) and for the out-of-plane C—H bending mode (up to 70 cm^{-1}). The frequencies of the in-plane C—C stretching mode also rise slightly (up to 10 cm^{-1}). It is, however, known that in the spectra of *d*-transition metal compounds containing π-ligands the in-plane C—C stretching mode always decreases on complexation [16]. Such a difference in the behaviour of the vibrational frequencies of the $C_8H_8^{2-}$ ligand coordination is probably due to the type of coordination in Cot complexes. Here the dative component of the coordination bond is practically absent, and the formation of a coordination bond leads to the transfer of electron density from the weakly bonding e_{2u} and e_{2g} ligand orbitals to the $5f_{\pm 2}$ and $6d_{\pm 2}$ metal orbitals, respectively [17]. It is known that the decrease in the vibrational frequencies of the ligand on coordination with metal is determined in general by the dative component of the metal—ligand bond, whose formation leads to the transfer of electron density from the metal to the antibonding ligand orbitals, as in the case of Cp and arene complexes of transition metals [16]. This accounts for the absence of a low-frequency shift of the in-plane C—C stretching bands, but not the observed fact that an increase in the frequencies of these modes takes place on coordination of the Cot ligand.

From the data given in Table 4, it follows that the impact of metal coordination on the vibrational frequencies of the Cot ligand is greater for the Th complex than for the La complex. Besides, as was mentioned above, the intensities of the IR bands of the ligand modes which appear in the spectra of the complexes due to the reduction of the ligand symmetry down to C_{8v}, are higher in the thoracene spectra than in that of the lanthanum complex.

No bands forbidden by the selection rules for the D_{8h} symmetry of the "free" $C_8H_8^{2-}$ dianion were observed in the Raman spectra of the La complex. Thus,

TABLE 4

FREQUENCIES OF ANALOGOUS VIBRATIONS IN THE SPECTRA OF Cot COMPLEXES AND K_2Cot

Assignment	Frequencies of vibrations (cm^{-1})		
	K_2Cot	KLaCot$_2$	ThCot$_2$
γ(CCC), E_{2g}	342	366	388
ρ(CH), A_{2u}	675	680	709
ν(CC), A_{1g}	735	742	747
ρ(CH), E_{1g}	710	771	774
β(CH), E_{1u}	880	891	895
β(CH), E_{2g}	—	—	—
ν(CC), E_{1u}	1295	1312	1314
ν(CC), E_{2g}	1490	1493	1497
ν(CH), E_{1u}	2994	3012	3014
ν(CH), E_{2g}	2979	—	2979
ν(CH), A_{1g}	3011	3039	3039

no band of the out-of-plane mode (ρ(CH), A_{1g}) and of the out-of-plane bending mode (χ(CCC), E_{2g}) were found in the Raman spectrum of the La complex, whereas these bands are seen in the Raman spectrum of thoracene (at 720 and 264 cm^{-1}, respectively). (A rise of the background, induced by fluorescence of the sample, and complicating recording of the weak lines, is observed in the Raman spectra of $KLaCot_2$ in the range above 800 cm^{-1}.)

Thus, the spectral data obtained by us are consistent with conclusion derived from the analysis of the physico-chemical properties of the Cot complexes of lanthanides, which have a more ionic metal—ligand bond compared to actinide complexes.

Skeletal modes

Six skeletal modes are possible for the Cot_2M molecule, with the following symmetry properties:

$$\Gamma = A_{1g} + A_{2u} + A_{1u} + E_{1g} + 2\,E_{1u},$$

two modes of which are allowed in the Raman spectrum (symmetrical stretching and degenerate tilt modes of the metal—ligand bond), three in the IR spectrum (antisymmetrical stretching and antisymmetrical tilt modes of the metal—ligand bond and the degenerate out-of-plane bending ligand—metal—ligand mode), and the torsional mode of class (A_{1u}) is forbidden in both spectra. In the absence of polarization data an unambiguous assignment of the observed Raman bands is hindered. However, in the case of thoracene, one may take advantage of the observed splitting pattern of the Raman bands. In a low-frequency range of the Raman spectrum of thoracene recorded at —180° C, two bands appear at 226 and 245 cm^{-1}; the first band is split into two components, the second into three. Owing to the fact that the lattice cell of the thoracene crystal contains only two formulae units [2] one can assign the 226 cm^{-1} band to the symmetrical metal—ligand mode, $\nu(ML)(A_{1g})$, and the 245 cm^{-1} band to the degenerate tilt, $\nu(ML)^{tilt}(E_{1g})$. The antisymmetrical analogs of these modes should be observed at higher frequencies range in the IR spectra. One strong band at 246 cm^{-1} was found in the IR spectrum in this range. It can be assigned to the $\nu(ML)(A_{2u})$ mode. With these assignments it is possible to calculate the force constant k(ML) in the linear three-atom model approximation. The value obtained, 4.25×10^6 cm^{-2}, appears to be close to those of the force constants of the metal—ligand bond calculated in the same approximation for the metallocene complexes Cp_2M (e.g. for ferrocene $k(ML) = 4.89 \times 10^6$ cm^{-2} [16]).

Still more difficult is the treatment of the low-frequency spectrum of the complex $KLaCot_2$. Two close-ranged lines 202 and 216 cm^{-1} are observed in the Raman spectrum in the frequency range of the metal—ligand modes. They can be assigned either to alternative modes, $\nu(ML)(A_{1g})$ and $\nu(ML)^{tilt}(E_{1g})$, or to the components of the $\nu(ML)(A_{1g})$ band splitting. However, for any of these plausible assignments the frequency of this $\nu(ML)(A_{1g})$ mode in the spectrum of $KLaCot_2$ lies lower than that in the spectrum of $ThCot_2$. The frequency of this mode is independent of the mass of the central metal atom, and it is determined only by the strength of the M—L bond. Therefore, the lower value of the ν(ML) frequency for the La complex in comparison with thoracene is in agreement with the greater strength of the coordination bond in the latter, in accord with available data.

References

1 A. Streitwiezer and U. Müller-Westehaft, J. Amer. Chem. Soc., 90 (1968) 7364.
2 A. Avdeef, K.N. Raymond, K.O. Hodgson and A. Zalkin, Inorg. Chemistry, 11 (1972) 1083.
3 E.C. Baker, G.W. Halstead and K.N. Raymond, Struct. Bonding (Berlin), 25 (1976) 23.
4 K.O. Hodgson and K.N. Raymond, Inorg. Chem., 11 (1972) 3030.
5 K.O. Hodgson and K.N. Raymond, Inorg. Chem., 11 (1972) 171.
6 A. Streitwiezer, U. Müller-Westehaft, G. Sonnichsen and F. Mares, J. Amer. Chem. Soc., 95 (1973) 8644.
7 R.G. Hayes and N. Edelstein, J. Amer. Chem. Soc., 94 (1972) 8688.
8 J.P. Clark and J.C. Green, J. Chem. Soc. Dalton, (1977) 505.
9 K.O. Hodgson, F. Mares, D.F. Starks and A. Streitwiezer, J. Amer. Chem. Soc., 95 (1973) 8650.
10 F. Mares, K. Hodgson and A. Streitwiezer, J. Organometal. Chem., 24 (1970) C68.
11 J. Goffart, J. Fuger, B. Gilbert, B. Kanellakopulos and G. Duyckaerts, Inorg. Nucl. Chem., Letters, 8 (1972) 403.
12 L. Hocks, J. Goffart, G. Duyckaerts and P. Teyssie, Spectrochim. Acta A, 30 (1974) 907.
13 A. Streitwiezer and N. Yoshida, J. Amer. Chem. Soc., 91 (1969) 7528.
14 V.T. Aleksanyan, I.A. Garbusova, T.M. Chernyshova and Z.V. Todres, J. Organometal. Chem., 201 (1980) 1.
15 G.M. Kuzyantz, A.O. Baronetsky, T.M. Chernyshova and Z.V. Todres, J. Organometal. Chem., 142 (1977) 139.
16 V.T. Aleksanyan and B.V. Lokshin, Vibrational spectra of π-complexes of transition metals. Series: Structure of molecules and chemical bond, Vol. 5, VINITI (Institute of Scientific and Technical Information, Academy of Sciences), Moscow, 1976.
17 N. Rosch and A. Streitwiezer, J. Organometal. Chem., 145 (1978) 195.