of 1:1 chelates of the metals with filled d orbitals, there is a general increase in ν^{CN} as the stability constant increases. On the other hand, the reverse trend is observed for the chelates of the elements with unfilled d orbitals (cobalt, nickel and copper). The increase in ν^{CN} with increasing stability constant is also observed for the 1:1 chelates of the transition metals chromium and iron, and those of the rare earths yttrium and lanthanum.

It must be finally emphasized that the correlations discussed in this paper can at best be only approximate and tentative, since the parameters chosen are rather arbitrary. Furthermore, in a strict sense, other factors such as the influence of N—metal bonding on the carboxylate frequency, as well as X-ray and thermodynamic data, must be considered before any meaningful conclusions can be drawn. These drawbacks do not, however, detract from the value of the i.r. method for structural elucidation of the NTA chelates, as discussed above.

SUMMARY

The following facts emerge from this study:

1. Infrared spectroscopy is a powerful tool for studying chelates of nitrilotriacetic acid in the crystalline state, because of the absence of solvent effects.

2. Initial evidence of chelation is provided by the shift in the CH_2 stretch of the NTA moiety, which generally decreases with increasing ionic radius of the metal.

3. The i.r. technique is particularly effective for distinguishing between the different types of bonding in which the carboxyl functions of NTA participate (—CO_2H, COO—metal, COO^-). Chelation is always accompanied by the appearance of an intense i.r. band in the 1684–1601 cm^{-1} region.

4. The 1:1 acid chelates of magnesium, strontium and barium—in contrast to that of calcium—exhibit a carboxylic acid absorption band, in addition to the COO—metal bands, and are characterized by the absence of a C—N band in 1130 cm^{-1} region. This suggests that the ligand is probably tridentate, instead of tetradentate, in these chelates.

5. The covalent or ionic nature of the COO—metal band can be roughly gauged from ν_a^{COOM}, this frequency increasing as the bonding becomes more covalent.

6. Confirmatory evidence for structural assignments, made on the basis of the different COO absorption bands, can be obtained from the position of the C—N stretching frequencies in the 1140–1100 cm^{-1} region. On chelation, this band is shifted to lower frequency with respect to Na_3NTA.

7. Correlations involving ν_a^{COOM}, $\nu_a^{COO^-}$, ν^{CN} and ionic radius or stability constant have been attempted. Certain trends are discernible but they cannot be unequivocally rationalized in view of the influence of other complicating factors.

A vibrational assignment for biscyclooctatetraenyl metal complexes

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Abstract—The structure of biscyclooctatetraenyl compounds (Ti, V, Th and U) is inferred from the results of i.r. spectra. We propose an assignment of the fundamental bands of these compounds based on qualitative results from the group theory. Some indications about the degree of ionicity of the metal ring bonds are also given.

INTRODUCTION

THE PURPOSE of this work is an assignment of the fundamental bands observed in the i.r. spectra of $(C_8H_8)_2Ti$, $(C_8H_8)_2V$, $(C_8H_8)_2Th$ and $(C_8H_8)_2U$, based on semi-empirical rules which allow us to predict the correct number and types of normal modes in the vibrational spectra, for a given symmetry.

In other words, we shall not be concerned here with the exact treatment of vibrational spectra by the "normal coordinate analysis." This analysis is too complicated for molecules containing a great number of atoms such as sandwich compounds. Nevertheless, a few complexes such as $(C_5H_5)_2Fe$ [1], $(C_5H_5)_2Ru$ [1], $(C_5H_5)_2Mg$ [2], $(C_6H_6)_2Cr$ [3, 4], $(C_6H_6)Cr(CO)_3$ [5], . . . have been treated in this way.

RX studies on these compounds give the following results:

In the solid state, the U and Th compounds [8, 9] show a D_{8h} symmetry, the two rings being bonded symmetrically to the metal.

On the opposite, the Ti compound [10] has not such a high symmetry: this molecule contains a symmetrically bonded ring (local symmetry C_{8v}), the other ring being asymmetrically bonded (local symmetry C_S). It is reasonable to suppose that the V compound has the same structure.

By means of the character table of these point groups, we can thus determine the normal vibration of these compounds. However, the intensities are sometimes too weak and a complete assignment is not always possible for an isolated compound. This difficulty has been overcome in this paper by investigation of series of four homologous compounds.

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[2] E. R. LIPPINCOTT, J. XAVIER and D. STEELE, *J. Am. Chem. Soc.* **83**, 2262 (1961).
[3] S. J. CYVIN, J. BRUNVOLL and L. SHÄFFER, *J. Chem. Phys.* **54**, 1517 (1971).
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[9] A. AVDEEF, K. N. RAYMOND, K. O. HODGSON and A. ZALKIN, *Inorg. Chem.* **11**, 1083 (1972).
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Experimental

These four complexes have been prepared by the method of Goffart *et al.* [6]. All spectra were recorded on solid samples (in KBr or KI pellets, or in nujol mulls) because the biscyclooctatetraenyl metal compounds are insoluble in/or react with nearly all good i.r. solvents. Infrared spectra are obtained with a Perkin–Elmer model 125 spectrophotometer in the range of 3500 to 400 cm^{-1} and a Beckman spectrometer has been used in the range 450–200 cm^{-1}.

Raman spectra were recorded with a modified Cary 81 apparatus [7] equipped with a He–Ne laser (110 mW at 6328 A°) and an Ar laser. Three of our complexes are very sensitive to the laser light; therefore, it has not been possible to record Raman spectra of $(C_8H_8)_2Ti$, $(C_8H_8)_2U$ and $(C_8H_8)_2V$.

Infrared spectra of biscyclooctatetraenyl uranium, thorium, titanium and vanadium are given in Figs. 1 and 4 and in Table 1.

The Raman spectrum of biscyclooctatetraenyl thorium has been recorded by Goffart [6].

Results and Discussion

(i) *Biscyclooctatetraenyl uranium and thorium*

Theoretical qualitative analysis of the vibrational motions for biscyclooctatetraenyl metals complexes of D_{8h} symmetry gives fifty-eight normal modes which belong to a reducible representation giving rise to the following decomposition:

$$\Gamma_{\mathrm{vibr}} = 4A_{1g} + 1A_{2g} + 2B_{1g} + 4B_{2g} + 5E_{1g} + 6E_{2g} + 6E_{3g}$$
$$+ 2A_{1u} + 4A_{2u} + 4B_{1u} + 2B_{2u} + 6E_{1u} + 6E_{2u} + 6E_{3u}.$$

Fifteen of the normal modes $(4A_{1g} + 5E_{1g} + 6E_{2g})$ are allowed as fundamentals in the Raman spectrum, and ten $(4A_{2u} + 6E_{1u})$ in the i.r. There are no coincidences, in agreement with the mutual exclusion rule. The thirty three remaining fundamentals are totally inactive.

The use of internal coordinates [11–13] of these molecules allows us to assign respective normal vibrations to the different irreducible representations of this point group. The results are given in Table 2. On the basis of semi-empirical results obtained with dicyclopentadienyl [1, 14], and dibenzene metals [15, 16], we have given a complete assignment of the i.r. spectra of $(C_8H_8)_2Th$ and U (Table 3).

Infrared spectra. The cyclooctatetraenyl dianion shows a very simple i.r. spectrum [15, 17] containing four normal vibrations: C—H stretching (E_{1u}, 2994 cm^{-1}), C—C stretching (E_{1u}, 1431 cm^{-1}), C—H bending(∥) (E_{1u}, 880 cm^{-1}) and C—H

[11] L. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations*. McGraw-Hill, New York (1955).
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[17] H. P. Fritz and H. Keller, *Z. Naturforsch.* **16b**, 231 (1961).

Table 1. Infrared spectra of biscyclooctatetraenyl titanium, vanadium, thorium and uranium*

$(C_8H_8)_2Ti$†	$(C_8H_8)_2V$†	$(C_8H_8)_2Th$†	$(C_8H_8)_2U$‡
260 vw	280 w	250 vs	237, 242 s
357 w	342 m	375 m§	385 m§
440 m	430 w		
	455 m	525 w	
	547 w	565 w	
		608 w	
625 w	626 w	642 w	
686 vs	688 vs	695 vs	698 vs
	724 w		
734 vs	748 vs	742 s	746 s
765 s	766 vs	775 s	777 m
784 m		790 w	792 m
800 w	800 w	810 w	
811 vs	809 vs		
	814 w	848 w	845 w
877 w	877 w		
905 w	899 w	895 s	900 s
1040 w	913 w		
	1295 w		
1325 w	1318 w	1315 m	1320 m
1433 m	1425 m	1430 m	—
1435 w	1435 w	1450 w	
	1460 w		
		1765 w§	1765 w§
1810 w		1865 w	1870 w
1955 w		1965 w	1960 w
		2830 w	
	2850 w	2880 w	
2920 m	2910 m	2920 m	—
3000 m	2990 m	3005 m	—

* Frequencies in cm^{-1}.
† Infrared spectra recorded in KBr and in KI pellets.
‡ Infrared spectrum recorded in nujol mulls, a reaction between $(C_8H_8)_2U$ and KBr having been observed by Goffart [6].
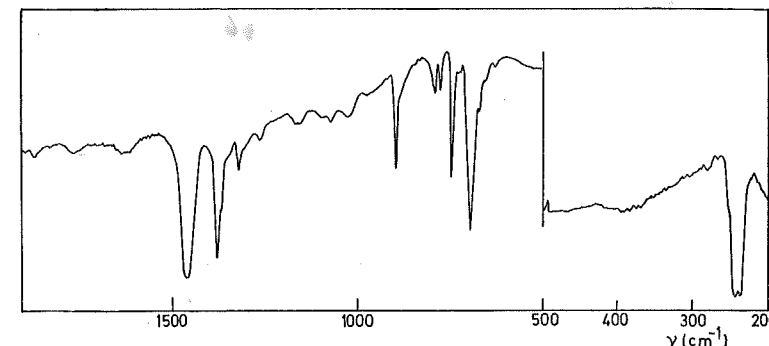§ Very broad bands.

Fig. 1. Infrared spectrum of $(C_8H_8)_2U$.

Table 2. Infrared and Raman active normal vibrations for D_{8h} symmetry

Irreducible representation	Approximate type of vibration*‡
4 A_{2u} (i.r. active)	C—H stretching
	C—C stretching
	C—H bending ($\perp$)
	asymmetric ring metal ring stretching
6 E_{1u} (i.r. active)	C—H stretching
	C—C stretching
	C—H bending ($\perp$) or CCC bending ($\perp$)†
	C—H bending ($\parallel$)
	ring metal ring bending
	asymmetric ring metal ring tilting
4 A_{1g} (Raman active)	C—H stretching
	C—C stretching
	C—H bending ($\perp$)
	symmetric ring metal ring stretching
5 E_{1g} (Raman active)	C—H stretching
	C—C stretching
	C—H bending ($\parallel$)
	C—H bending ($\perp$) or CCC bending ($\perp$)†
	symmetric ring metal ring tilting
6 E_{2g} (Raman active)	C—H stretching
	C—C stretching
	C—H bending ($\parallel$)
	C—H bending ($\parallel$)
	C—H bending ($\perp$)
	CCC bending ($\perp$)

* $\parallel$ and $\perp$ define the direction of the nuclear displacements with respect to the C_8H_8 plane ring.

† Our qualitative analysis cannot distinguish between these two possibilities. For an unambiguous interpretation, it would be necessary to use the GF matrix method (see Ref. [13]).

‡ Normal skeletal vibrations are given by Fritz [15].

bending ($\perp$) (A_{2u}, 684 cm^{-1}). We see that the fourth normal mode is greatly influenced by coordination: it undergoes a shift of about 160 cm^{-1} to higher frequencies (Table 3). This shift is interpreted in the following way with respect to free cyclo-octatetraene: the normal "out of plane" vibrations are more difficult when metal orbitals interact with ring orbitals. On the other hand, the "in plane" normal vibrations are not very much sensitive to coordination. Moreover, the difference in frequencies observed between the two C—H or C—C modes is explained by the "in phase" and "out of phase" vibration between the two rings [15].

The ring metal ring normal vibrations are generally observed below 700 cm^{-1} and have been assigned as follows:

The asymmetric ring metal ring tilting vibration is always given at the highest frequency for all metal sandwich compounds [15]. It would seem reasonable to assign the 695 cm^{-1} band to such a vibration but this high frequency seems abnormal

Table 3. Infrared assignment of biscyclooctatetraenyl uranium and thorium for a D_{8h} symmetry*

$(C_8H_8)_2$Th	$(C_8H_8)_2$U	Assignment	Irreducible representation
3005	—†	C—H stretching	$A_{2u}, E_{1u,}$
2920	—†		
1430	—†	C—C stretching	A_{2u}, E_{1u}
1315	1320		
895	900	C—H bending ($\parallel$)	E_{1u}
775	777	C—H bending ($\perp$) and	A_{2u}, E_{1u}
742	746	C—H bending ($\perp$) or CCC bending ($\perp$)	
695	698	asymmetric ring metal ring tilting	E_{1u}
250	240	asymmetric ring metal ring stretching	A_{2u}
(125)‡	(145)‡	ring metal ring bending	E_{1u}

* Frequencies in cm^{-1}.

† The C—H and C—C stretching normal modes are not given because i.r. spectra of the uranium compound has been taken in nujol mulls only.

‡ Calculated values (see text).

compared to biscyclopentadienyl and dibenzene metals and we cannot actually explain this fact.

The ring metal ring stretching band is observed at 240–250 cm^{-1}; in the case of $(C_8H_8)_2$U, this band is more complex (Fig. 1) and this fact can be explained by an interaction between this normal mode and the monoclinic lattice vibrations.

The remaining fundamental band (ring metal ring bending) is generally observed below 200 cm^{-1} [15]. It would be necessary to record the IR spectra below 200 cm^{-1} to observe such a normal vibration.
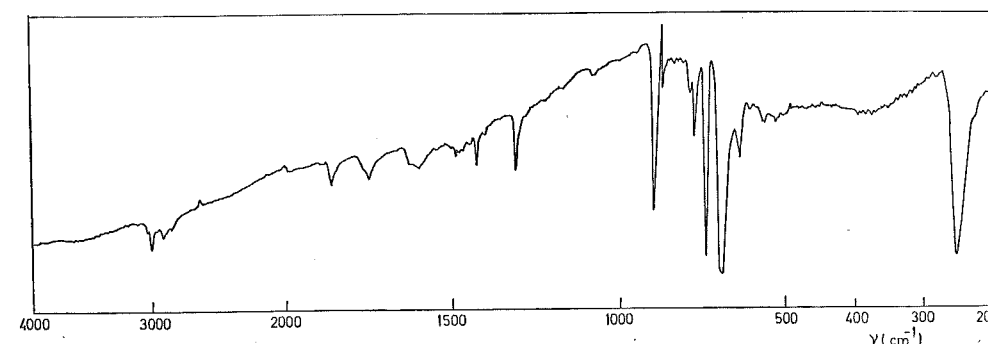
Fig. 2. Infrared spectrum of $(C_8H_8)_2$Th.

4

Nevertheless, we observe a very broad band in the region 350 to 400 cm^{-1} (Table 1 and Figs. 1, 2) and this band could be assumed as a combination of the ring metal ring stretching and the ring metal ring bending normal vibrations. From such an interpretation, the expected ring metal ring bending normal mode can be calculated (Table 3).

Raman spectra. For a complete assignment of the normal vibrations of these compounds, it would be necessary to have Raman spectra with polarization measurements. Unfortunately, the U compound is destroyed by the laser light and we have recorded the Raman spectrum of $(C_8H_8)_2$Th only [6]. From this spectrum only, it is hazardous to ascribe completely the Raman lines. Nevertheless, we can assign the 225 and 242 lines to symmetric ring metal ring stretching and symmetric ring metal ring tilting respectively. These assignments result from empirical comparisons with Raman spectra of ferrocene [1, 14] dibenzene chrome [18] and dibenzene chromium cation [18].

(2) *Biscyclooctatetraenyl vanadium and titanium*

The vibrational analysis of the (C_8H_8)—M system (C_{8v} symmetry) gives twenty eight normal modes:

$$\Gamma_{vibr} = 4A_1 + 1A_2 + 2B_1 + 4B_2 + 5E_1 + 6E_2 + 6E_3$$

with nine i.r. active ($4A_1 + 5E_1$) normal vibrations (Table 4).

The assignments are based on the same considerations as for the U and Th compounds. Nevertheless, we have only two skeletal normal vibrations: a ring

Table 4. Infrared assignment for (C_8H_8)Ti and (C_8H_8)V for a C_{8v} symmetry*

(C_8H_8)Ti	(C_8H_8)V	Assignment	Irreducible representation
3000	2990	C—H stretching	A_1, E_1
2920	2910		
1433	1425	C—C stretching	A_1, E_1
1325	1318		
811	809	C—H bending ($\parallel$)	E_1
765	766	C—H bending ($\parallel$) and	
734	748	C—H bending ($\perp$) or CCC bending ($\perp$)	A_1, E_1
686	688	Asymmetric ring Metal tilting	E_1
440	455	Asymmetric ring metal stretching	A_1

* Frequencies in cm^{-1}.

[18] H. P. Fritz, W. Lüttke, H. Stammreich and R. Forneris, *Spectrochim. Acta* 17, 1068 (1961).
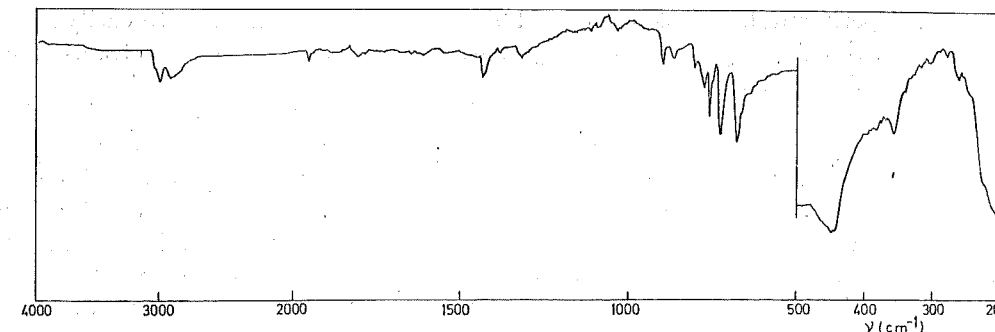

Fig. 3. Infrared spectrum of $(C_8H_8)_2$Ti.

metal stretching (A_1) and a ring metal tilting (E_1). For a C_{8v} point group, we should have, of course, no ring metal ring bending vibration. The coordination of the second asymmetrical ring induces such a vibration and gives, in addition, a more complicated spectrum (Figs. 3 and 4).

The intensities of these skeletal vibrations allow us to get some information about the ionicity of the ring metal bond. These absorption bands do not exist for pure ionic compounds (see, for instance, the i.r. spectrum of $(C_8H_8)^=K_2^+$). The Ti and V compounds having weak skeletal vibrations* are consequently more ionically bonded than Th and U compounds which have strong skeletal vibrations. These results are in agreement with the relative ease of sublimation of these compounds, ionic sandwich compound being not sublimated easily [15, 19]†; we have indeed
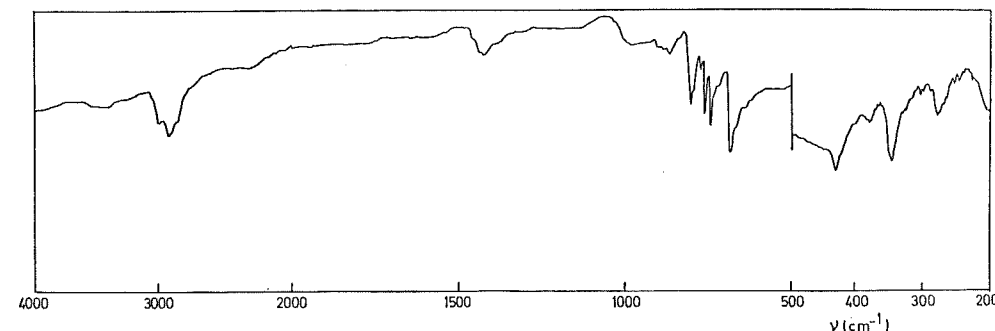

Fig. 4. Infrared spectrum of $(C_8H_8)_2$V.

* Note that the intensity of the asymmetric ring metal ring tilting decreases less than the others. This fundamental band depends not very much of the nature of the ring metal bond.
† It seems that this experimental observation in not general. Nugent [20] and Cotton [21] have indeed sublimated ionic cyclopentadienyl compounds.

[19] F. Mares, K. Hodgson and A. Streitwieser Jr. *J. Organometall. Chem.* 24, C 68 (1970).
[20] L. J. Nujent, P. G. Laubereau, G. K. Werner and K. N. Vander Sluis, *J. Organometall. Chem.* 27, 365 (1971).
[21] F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.* 80, 269, (1958).

observed, experimentally, that the U and Th compounds can sublimate easily; on the opposite, the V compound is destroyed with removal of free cyclooctatetraene when temperature is increased.

Conclusions

It seems that a rigorous D_{8h} symmetry does not exist in the transition metals complexes having $3d$ orbitals. For actinides, this structure is more probable, considering that U and Th have very large $5f$ and $6d$ orbitals allowing a good overlap with ring π orbitals. In the case of Ti and V, this overlap is weak and we can conclude, from the degree of ionicity of the bond, that the two rings are more electrostatically bonded than for the U and Th compounds.

The present semi-empirical approach is useful to give an approximate picture of the structure of these molecules; however, it would be interesting now to treat this problem by the "normal coordinate analysis" which allow to calculate the exact frequencies of the different vibration modes of the complete molecule.

Biscyclopropylidene: the case of the missing double-bond Raman frequency*

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Abstract—In numerous derivatives of biscyclopropylidene, $(CH_2)_2C=C(CH_2)_2$, the double-bond frequency expected in the range 1600–2000 cm^{-1} in the Raman effect failed to appear. To study the cause of this absence, the i.r. spectra of solid, liquid and gaseous biscyclopropylidene have been observed in the region 4000–50 cm^{-1}, and Raman spectra of the liquid phase have also been recorded at high gain. The 32 allowed vibrations have been assigned on the basis of a D_{2h} molecular structure, and a normal-coordinate calculation carried out with a modified Urey–Bradley force-field. The anomalously weak Raman intensity of the double-bond vibration has been interpreted by means of a bond polarizability theory for tetra-substituted double-bonds. The theory accounts for the difference in the observed intensities in the double-bond Raman lines in biscyclopropylidene and tetramethylethylene and is used to predict intensities for this line due to other alkyl-substituted double-bonds.

Introduction

In this laboratory over the past several years we have obtained the Raman spectra of bi(bicyclo(4.1.0)heptylidene) (*1*), octamethylbiscyclopropylidene (*2*) 2,2,2′,2′-tetramethylbiscyclopropylidene (*3*), and 2,2,3′,3′-tetramethylbiscyclopropylidene (*4*), whose structural formulae are shown in Fig. 1. No conclusive evidence for a frequency corresponding to the expected double-bond vibration was found in any of these spectra.

Since the frequency of the double-bond vibration in ethylene occurs at 1623 cm^{-1}, and that in methylenecyclopropane [1, 2] at 1736 cm^{-1}, the same vibration in biscyclopropylidenyl derivatives would be expected by linear extrapolation to fall somewhere near 1850 cm^{-1}. At high gains several very weak peaks are observed in the region 1800–1900 cm^{-1} but no one of these can be assigned with confidence to the double-bond vibration.

Du Laurens *et al.* [3] observed the Raman spectra of *3* and *4* and assigned a weak polarized line at 1751 cm^{-1} in the spectrum of *3* to an A_1 fundamental. However, in view of the location of the frequency at 1736 cm^{-1} in methylenecyclopropane, a value of 1751 seems much too low for the double-bond vibration in *3* and it is probably due to an overtone or combination transition. Du Laurens *et al.* did

[1] R. W. Mitchell and J. A. Merritt, *Spectrochim. Acta* **27A**, 1609 (1971).
[2] J. E. Bertie and M. G. Norton, *Can. J. Chem.* **48**, 3889 (1970).
[3] B. du Laurens, A. Bezaguet, G. Davidovics, M. Bertrand and J. Chouteau, *Bull. Soc. Chim. France* 799 (1967).