Inorganica Chimica Acta, 11 (1974) 5–8
© ELSEVIER Sequoia S.A., Lausanne – Printed in Switzerland

Infrared Band Assignments of Coordinated C_6Cl_5 in Compounds of the Type $[MX(C_6Cl_5)(PPh_3)_2]$

J. CASABO, J. M. CORONAS and J. SALES
Department of Inorganic Chemistry, Faculty of Science, University of Barcelona, Spain

Received February 16, 1974

A review of the C_6Cl_6 infrared spectrum is made and some combination bands observed in this spectrum are assigned. On the basis of the C_6Cl_6 spectrum, band assignments for some new compounds of the $[MX(C_6Cl_5)(PPh_3)_2]$ type (with M = Ni, Pd; X = Cl, Br, I, NCS, NCO, N_3) are proposed.

Introduction

Complexes of the $[MX(C_6Cl_5)(PR_3)_2]$ type with M = Ni, Pd; X = halide or pseudohalide and R = Et, Ph, have been described.[1–4] One of us[5] has prepared compounds of the same type with M = Ni, and X = NCS, NCO, N_3; M = Pd and X = Cl, Br, I, NCS, NCO, N_3 and R = Ph for all of them. Analytical data for these new compounds are given in Table I.

Rausch *et al.*[4] observed some bands in the infrared spectra of these compounds attributable to the coordinated C_6Cl_5 group. These authors, however, attempted no assignment of bands. These assignments must be supported in the previous assignments of the bands observed in the infrared spectrum of C_6Cl_6.

Kopelman and Schnepp[6], with an approximate normal-coordinate calculation and assuming the molecule planar, made the first attempt to assign the infrared bands of solid C_6Cl_6 in the 4000–600 cm^{-1} zone. Since it had been experimentally shown that the molecule is not planar in the vapor state, Kopelman studied the assignments assuming D_{3d} symmetry (even when X-ray diffraction studies had not shown that the molecule was not planar in the solid state). Saeki[7], on the basis of D_{6h} symmetry and with semiempirical considerations about the infrared (in the gaseous state) and Raman spectra of C_6Cl_6, makes an assignment of bands. Delorme and co-workers[8,9] when comparing the infrared spectra of the C_6X_6 type molecules in the solid state observe the apparition of additional bands of increasing intensity with the atomic weight of the halogen. This is attributable to an increasing loss of planarity going from C_6F_6 to C_6I_6, so that C_6Cl_6 should be already considered belonging to point group D_{3d}.

TABLE I. Analytical Data.

Compound	Found (%)					Calculated (%)				
	C	H	Cl	Br or N	Ni or Pd	C	H	Cl	Br or N	Ni or Pd
$[NiCl(C_6Cl_5)(PPh_3)_2]$[a]	58.5	3.6	23.8	–	6.6	58.07	3.48	24.50	–	6.76
$[NiBr(C_6Cl_5)(PPh_3)_2]$[a]	55.2	3.2	19.6	8.8	6.3	55.24	3.31	19.42	8.75	6.43
$[NiI(C_6Cl_5)(PPh_3)_2]$[a]	52.9	3.5	18.7	–	6.0	52.55	3.15	18.47	–	6.12
$[Ni(NCS)(C_6Cl_5)(PPh_3)_2]$	57.4	3.6	20.1	1.5	6.4	57.95	3.40	19.90	1.57	6.59
$[Ni(NCO)(C_6Cl_5)(PPh_3)_2]$	59.7	3.7	20.0	1.5	6.6	58.97	3.45	20.24	1.60	6.71
$[NiN_3(C_6Cl_5)(PPh_3)_2]$	58.1	3.4	20.2	4.6	6.6	57.64	3.45	20.24	4.81	6.71
$[PdCl(C_6Cl_5)(PPh_3)_2]$	54.8	3.4	23.0	–	11.3	55.00	3.32	23.22	–	11.62
$[PdBr(C_6Cl_5)(PPh_3)_2]$	53.0	3.2	18.2	8.7	11.2	52.47	3.15	18.44	8.32	11.80
$[PdI(C_6Cl_5)(PPh_3)_2]$	49.9	2.9	17.4	–	10.1	50.10	3.01	17.60	–	10.33
$[Pd(NCS)(C_6Cl_5)(PPh_3)_2]$	54.4	3.3	18.8	1.6	11.2	55.02	3.22	18.90	1.49	11.34
$[Pd(NCO)(C_6Cl_5)(PPh_3)_2]$	57.0	3.4	19.1	1.5	11.3	55.95	3.28	19.22	1.52	11.54
$[PdN_3(C_6Cl_5)(PPh_3)_2]$	54.3	3.3	19.0	4.4	11.3	54.65	3.28	19.21	4.55	11.53

[a] Compounds previously reported.[3]

TABLE II. Infrared Spectral Data of C_6Cl_6.

Observed Frequencies (cm^{-1})	Assignment
1715 vw[a]	$(\nu_{13}+\nu_{12})(E_u)$
1440 w[a]	$(\nu_1+\nu_{14})(E_u)$
1392 vw[b]	$(\nu_1+\nu_4)(A_{2u})$
1340 vs[a]	$\nu_{13}(E_u)$(6)(7)(9)
1295 s[a]	$\nu_6(A_{2u})$(6)(9)
1215 vw[a]	$\nu_1(A_{1g})$(7)
1105 w[a]	$(\nu_5+\nu_2)(A_{2u})$
1062 vw[b]	$(\nu_5+\nu_{17})(E_u)$
965 vw[a]	$(\nu_{13}+\nu_2)(E_u)$
930 w[a]	$(\nu_5+\nu_{11})(E_u)$
820 vw[b]	$(\nu_{15}-\nu_{12})(A_{1u}+A_{2u}+E_u)$
790 vw[a]	$(\nu_{19}+\nu_{11})(A_{1u}+A_{2u}+E_u)$
720 m[a]	$\nu_5(A_{2u})$(6)(9)
695 vs[a]	$\nu_{12}(E_u)$(6)(7)(9)

[a] Bands observed in this work. [b] Bands not observed in this work, but reported in the literature.[9]

The frequencies observed in the infrared spectrum of solid C_6Cl_6 are listed in Table II (range 4000–250 cm^{-1}), together with the corresponding assignments according to the literature.

The bands at 1295 and 720 cm^{-1}, assigned to the ν_6 and ν_5 vibrations, respectively, might also be assigned to the ν_{19} (E_u) and ν_{20} (E_u) modes, but since we have observed no splitting of the bands upon coordination of the C_6Cl_5 group in the complexes, the assignment given above seems more convenient.

Although several authors[6,9] report weak absorptions in the C_6Cl_6 infrared spectrum (probably due to combination bands), no attempt has been made to assign them in the point groups D_{3d} or D_{6h}. Assuming no planarity of the C_6Cl_6 molecule, with the assignments of fundamental vibrations previously given above, and on the basis of selection rules of overtones and combination bands of D_{3d} symmetry, the weak remaining bands observed in the spectrum of C_6Cl_6 have been assigned as indicated in Table II.

Normal Modes Analysis of Coordinated C_6Cl_5

Coordinated C_6Cl_5 group belongs to point group C_s. Churchill and Veidis[11] have shown with X-ray diffraction techniques that the chlorine atoms of the C_6Cl_5 group are not on the plane of the aromatic ring in the compound $[Ni(C_6F_5)(C_6Cl_5)(PPh_2Me)_2]$, in spite of the fact that the fluorine atoms of the C_6F_5 group can be considered on the mentioned plane.

The correlations in Table III are inferred from the character tables of point groups D_{3d} and C_s.

The $3A_{2u}+5E_u$ modes will remain infrared active upon coordination of the C_6Cl_5 group, and the doubly degenerate modes must split into two components ($A'+A''$) both of them infrared active. In addition, the forbidden bands which become infrared active in the C_s group should also appear in the spectrum.

TABLE III. Correlation Diagram and Spectral Activity of Normal Modes of Vibration.

D_{3d}	C_s	Normal Modes of Vibration	Frequencies of C_6Cl_6 (cm^{-1})
A_{1g}(R)	A'(R,IR.)	ν_1	1225
		ν_2	372
A_{2g}	A''(R,IR.)	ν_3	–
		ν_4	172
A_{2u}(IR)	A'(R,IR.)	ν_5	720
		ν_6	1295
A_{1g}(R)	A'(R,IR.)	ν_7	704
		ν_8	97
A_{1u}	A''(R,IR.)	ν_9	–
		ν_{10}	–
E_g(R)	A'(R,IR.)+A''(R,IR.)	ν_{11}	213
		ν_{15}	1522
		ν_{16}	–
		ν_{17}	340
		ν_{18}	322
E_u(IR.)	A'(R,IR.)+A''(R,IR.)	ν_{12}	694
		ν_{13}	1340
		ν_{14}	217
		ν_{19}	594
		ν_{20}	80

Results and Discussion

The infrared spectra of the $[MX(C_6Cl_5)(PPh_3)_2]$ type complexes studied in this paper (Figure 1) show together with the bands due to triphenylphosphine[12], other bands which may be assigned to coordinated C_6Cl_5. The bands due to M–X and M–C vibrations can also be observed by increasing the concentration of the nujol mulls. The bands due to M–P vibrations are not observed, since they appear beyond the frequency range studied in this work.[13] The frequencies attributed to the C_6Cl_5 group together with the proposed assignments, are given in Table IV.

Five vibrations belonging to the $E_u(D_{3d})$ species should appear in the infrared spectrum of C_6Cl_6. In fact, only three are observed, at 1340 cm^{-1} (ν_{13}), 695 cm^{-1} (ν_{12}) and 217 cm^{-1} (ν_{14}). The two other bands, calculated at 594 cm^{-1} (ν_{19}) and 80 cm^{-1} (ν_{20})[10] have never been observed in the infrared spectrum of C_6Cl_6.

The splitting of the ν_{13} frequency is very clearly observed in the complexes studied, as it must be with a doubly degenerate mode. A shift of such vibrations towards lower frequencies is observed, but there are

Figure 1. Infrared Spectra of: a) $[NiI_2(PPh_3)_2]$ (KBr disk); b) C_6Cl_6 (KBr disk); c) $[NiNCOC_6Cl_5(PPh_3)_2]$ (Nujol mull).

TABLE IV. Infrared Spectral Data.

Compounds	ν(M–X)	ν(M–C)	$\nu_{13}(E_u)$	$\nu_6(A_{2u})$	$\nu_1(A_{2g})$	$\nu_5(A_{2u})$	$\nu_{12}(E_u)$
C_6Cl_6	–	–	1340	1295	1225 (R)	720	695
$[NiCl(C_6Cl_5)(PPh_3)_2]$	360–340	587	1328–1318	1288	1230	–	670
$[NiBr(C_6Cl_5)(PPh_3)_2]$	305	583	1322–1312	1282	1228	–	668
$[NiI(C_6Cl_5)(PPh_3)_2]$	–	581	1322–1312	1282	1228	–	670
$[NiNCS(C_6Cl_5)(PPh_3)_2]$	360	585	1322–1312	1285	1225	–	668
$[NiNCO(C_6Cl_5)(PPh_3)_2]$	400	588	1328–1318	1288	1230	–	670
$[NiN_3(C_6Cl_5)(PPh_3)_2]$	400	587	1325–1315	1288	1230	–	670
$[PdCl(C_6Cl_5)(PPh_3)_2]$	305	583	1328–1318	1288	1228	–	670
$[PdBr(C_6Cl_5(PPh_3)_2]$	250	580	1328–1318	1285	1225	–	670
$[PdI(C_6Cl_5)(PPh_3)_2]$	–	579	1328–1318	1288	1226	–	670
$[PdNCS(C_6Cl_5)(PPh_3)_2]$	298	582	1328–1318	1288	1224	–	670
$[PdNCO(C_6Cl_5)(PPh_3)_2]$	350	582	1328–1318	1288	1224	–	670
$[PdN_3(C_6Cl_5)(PPh_3)_2]$	360	580	1328–1318	1285	1224	–	670

no large differences upon changing the nature of the other ligands or even of the central atom.

The ν_{12} vibration should split into two infrared active components. Such splitting has not been observed in the complexes studied in this paper, due to the fact that one of the components is overlapped with the v[Φ(C–C)] vibration of triphenylphosphine[12], appearing with strong intensity at 692 cm^{-1}; the other component is observed at 670 cm^{-1}. A shift of the latter frequency is also observed upon coordination of C_6Cl_5, without large differences whatever the nature of the other ligands or that of the central atom. The ν_{14} vibration is not observed because it appears at 217 cm^{-1}, beyond the frequency range studied in this work.

Two of the three $A_{2u}(D_{3d})$ vibrations for C_6Cl_6 are observed at 1295 cm^{-1} (ν_6) and at 720 cm^{-1} (ν_5). The third one, assigned by Delorme to $\nu_4(A_{2u})$[7], appears at 172 cm^{-1}, beyond the studied range. The fact that the infrared spectrum of C_6Cl_6 exhibits these two well-defined bands of medium intensity, confirms that there is some lack of planarity, since progressive distortion of $D_{6h} \rightarrow D_{3d}$ symmetry leads to the apparition of the two new bands $[B_{1u}(D_{6h}) \rightarrow A_{2u}(D_{3d})]$ which are active in the latter group. In the complexes studied, a band attributable to the ν_6 vibration of coordinated C_6Cl_5, is observed at about 1285 cm^{-1}. A shift towards lower frequencies is also observed, without large differences upon changing the nature of the coordinated groups or that of the central ion. The other frequency, appearing at 720 cm^{-1} in hexachlorobenzene, cannot be observed in the compounds studied due to overlapping with the v[Φ(C–C)] and r(X-sensible) frequencies of coordinated triphenylphosphine appearing at 692 and 700–705 cm^{-1}.[12] However, a very weak band sometimes appears at 710 cm^{-1}.

All of the complexes studied exhibit a well defined band of medium intensity at 1225–1230 cm^{-1}, which can be assigned to the $\nu_1(A_{1g})$ vibration of the D_{3d} group. This Raman active but infrared inactive vibration, observed by Saeki at 1225 cm^{-1} for C_6Cl_6, becomes infrared active in the coordinated C_6Cl_5 group, and belongs to the $A'(C_s)$ species. The second band, at 372 cm^{-1}, assigned by Saeki to $\nu_2(A_{1g})$, is not clearly observed in the infrared spectra of the products studied here; however, weak and poorly defined bands are sometimes observed at 350–360 cm^{-1}, on of which might well be assigned to this vibration. On the other hand, the fact that the M–X vibrations appear in this zone, makes the assignments of these frequencies difficult.

Another defined band of medium intensity is observed at 575–590 cm^{-1} in all of the products studied in this work. This band might well be assigned to the $\nu_{19}(E_u)$ vibration of C_6Cl_6, calculated by Scherer at 594 cm^{-1};[10] the fact that no band is observed at this frequency, and that the band observed in this region in the spectra of the compounds studied here shows no splitting, does not allow such assignment. This band, however, may be assigned to the M–C vibration. The fact that the M–C_6Cl_5 bond length has been found shorter than that of M–C_6F_5[11] justifies the proposed assignment, in spite of the fact that no bands, attributable to this vibration in analogous compounds with pentafluorophenyl, have been observed by Goggin and Goodfellow.[14]

Experimental

Infrared Spectra

The spectra from 4000 cm^{-1} to 250 cm^{-1} were measured on a Beckman IR–20A infrared spectrophotometer calibrated with polystyrene film. Samples were studied as nujol mulls between CsBr plates. The frequencies are accurate to ± 2 cm^{-1}.

Preparation of the Compounds

The compounds already known, whose infrared spectra are considered here, have been obtained by procedures given in the literature.[3] The new compounds prepared by us have been obtained following a procedure given elsewhere.[5]

Analysis

Microanalytical determinations of C, H, N and halogens were performed at the "Instituto de Química Orgánica de Barcelona (C.S.I.C.)". Niquel and palladium were determined gravimetrically with dimethylglyoxime after destruction of the complexes with boiling nitric and sulphuric acids.

References

1 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

2 M. D. Rausch and F. E. Tibbetts, *Inorg. Chem.*, *9*, 512 (1970).

3 K. MacKinnon and B. O. West, *Aust. J. Chem.*, *21*, 2801 (1968).

4 M. D. Rausch, F. E. Tibbetts and H. B. Gordon, *J. Organometal. Chem.*, *5*, 493 (1966).

5 J. Sales, *Thesis*, Barcelona (1973).

6 R. Kopelman and O. Schnepp, *J. Chem. Phys.*, *30*, 597 (1959).

7 S. Saeki, *Bull. Chem. Soc. Japan*, *35*, 322 (1962).

8 P. Delorme, V. Lorenzelli and M. Fournier, *Comp. Rend.*, *259*, 751 (1964).

9 P. Delorme, F. Deniselle and V. Lorenzelli, *J. Chem. Phys.*, *64*, 592 (1967).

10 J. Scherer, *Spectrochim. Acta*, *23A*, 1489 (1967).

11 M. Churchill and M. Veidis, *Chem. Comm.*, 1099 (1970).

12 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, *24A*, 845 (1968).

13 K. Nakamoto, "Infrared spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y. (1970).

14 L. Goggin and R. S. Goodfellow, *J. Chem. Soc. (A)*, 1462 (1966).