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THE PREPARATION AND INFRA-RED SPECTRA OF PHTHALOCYANINE DERIVATIVES OF THE PLATINUM-GROUP METALS

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Abstract—The i.r. spectra of phthalocyanine derivatives of Pd, Pt, Rh, Ir, Ru, Os in the region 220–5000 cm^{-1} are reported. The mono (1,2-dicyanobenzene) adducts, PcCl. Ir(III) Cl·C_6H_4 $(CN)_2$, Pc* MCl·C_6H_4 $(CN)_2$ (M = Ru(III), Os(III)), are found to be the main reaction products of Ir, Ru, Os chlorides and 1,2-dicyanobenzene at ca. 280°C. Osmium tetroxide, OsO_4, and 1,2-dicyanobenzene give, at the same reaction temperature, the (phthalocyanino) dioxo-osmium(VI)–1,2-dicyanobenzene adduct, $PcOsO_2·C_6H_4(CN)_2$.

Bands relatively sensitive to and characteristic of the platinum-group metals in their phthalocyanines are observed. One possible tentative assignment of the weak band varying between 910–918 cm^{-1} is as a rocking vibration of the metal-phthalocyanine nucleus.

INTRODUCTION

Platinum-group metal phthalocyanines

THE REACTION of palladium(II), platinum(II) chlorides with excess 1,2-dicyanobenzene, $C_6H_4(CN)_2$, at 280°C gives well-characterized (monochlorophthalocyanino) palladium (II),(1) PdPcCl, and (phthalocyanino) platinum(II),(2) PtPc. However the products of reaction of the chlorides of Rh(III),(3) Ir(III),(3) Ru(III),(7) Os(IV)(3) (as complex $(NH_4)_2(OsCl_6)$) with excess 1,2-dicyanobenzene at elevated temperatures are much less certain. Consequently the preparations and purifications of these products were re-examined.

Detailed temperature study of the reaction between hydrated $RuCl_3$ and 1,2-dicyanobenzene and extension of the purificative methods showed that paramagnetic $PcRuCl·C_6H_4(CN)_2$ was formed predominantly at 290°C. This reaction is reported(7) to give largely metal-free phthalocyanine, PcH_2. The corresponding reaction with *o*-cyanobenzamide, $C_6H_4(CONH_2)(CN)$, reported as giving crude PcRu(II),(5) gave $PcRuCl·C_6H_4(CONH_2)(CN)$. Hydrated $IrCl_3$ and $(NH_4)_2(OsCl_6)$ reacted with $C_6H_4(CN)_2$ to give the adducts $PcCl·IrCl·C_6H_4(CN)_2$, $PcOsCl·C_6H_4(CN)_2$. $RhCl_3·3H_2O$ failed to react with excess $C_6H_4(CN)_2$ at 280°C to give (phthalocyanino) chlororhodium

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* Pc, the phthalocyanino residue, $C_{32}H_{16}N_8$
PcCl, the monochlorophthalocyanino group, $C_{32}H_{15}ClN_8$

(1) P. A. BARRETT, D. A. FRYE and R. P. LINSTEAD, *J. Chem. Soc.* 1157 (1938).

(2) P. A. BARRETT, C. E. DENT and R. P. LINSTEAD, *J. Chem. Soc.* 1719 (1936).

(3) W. HERR, *Z. Naturforsch.* **9a**, 180 (1954).

(4) B. D. BEREZIN, *Dokl. Akad. Nauk SSSR* **150**, 1039 (1963).

(5) P. C. KREUGER and M. E. KENNEY, *J. Inorg. Nucl. Chem.* **25**, 303 (1963).

(6) B. D. BEREZIN and N. I. SOSNIKOVA, *Dokl. Akad. Nauk. SSSR* **146**, 604 (1962).

(7) P. C. KREUGER, Ph.D. Thesis, University Microfilms No. 64–14. 77.

(III), PcRhCl, as reported.(4) The desired product was formed, however, on using $C_6H_4(CONH_2)(CN)$ in the synthesis.

The reaction product of OsO_4 and $C_6H_4(CN)_2$ at 280°C has been extracted with and reprecipitated from concentrated sulphuric acid. It has been characterized as the diamagnetic polymer $(PcOs(IV)\ O{\cdot}SO_2{\cdot}O)_n$.(6) The present work shows the main reaction product, before sulphuric acid extraction, to be the paramagnetic (phthalocyanino) dioxo-osmium(VI) dicyanobenzene adduct, $PcOsO_2{\cdot}C_6H_4(CN)_2$.

The $C_6H_4(CN)_2$ present in these derivatives can only be removed by extremely strong heating when it slowly sublimes giving a colourless deposit. This molecule may be regarded as solvating the phthalocyanines of Ir, Ru, Os, the syntheses being carried out in molten $C_6H_4(CN)_2$ as solvent. It can be replaced by boiling the "solvates" with organic bases to give products such as $M\ Pc{\cdot}nC_6H_5NH_2$ ($M = Ir(II)$, $n = 6$,(8) $M = Ru(II)$, $n = 2$(8) or 6(5)), $PcOsO_2{\cdot}3C_6H_5NH_2$(8) and $PcRuCl{\cdot}nC_5H_5N$($n = 4$ to 5).(8) In most cases the IR spectra of the dicyanobenzene solvates exhibit a C≡N stretching frequency of weak intensity at 2220 ± 10 cm^{-1}. (Table 1).

The chlorine directly bound to trivalent Rh, Ir, Ru, Os in their phthalocyanines may be replaced on heating with concentrated sulphuric acid giving volatile HCl or slowly precipitated as silver chloride by the action of hot, concentrated nitric acid and silver nitrate. Reaction with boiling organic bases effectively reduces the central metal atom removing its chlorine. Nuclear chlorine in the phthalocyanino residue can be removed by the Carius method using fuming nitric acid and silver nitrate at high temperature and pressure.

SPECTRA

Although phthalocyanine derivatives of Pd,(1) Pt,(2) Rh,(3,4) Ir,(3) Ru,(5) Os,(3,6) have been described, IR spectra are only reported for Ru(5) complexes. Thus bands useful for the identification of (phthalocyanino) ruthenium (II), its hexa-aniline and hexa-*o*-toluidine adducts in the 650–1150 cm^{-1} region in Nujol suspension are given.

The IR spectra of PcH_2,(9) M Pc(10)(M = Cu(II), Co(II), Ni(II), Zn(II)) have been studied in Nujol suspension and showed that the two major polymorphic modifications* of the phthalocyanines can be distinguished by their spectra. The absorption spectra of sublimed layers of PcH_2, M Pc (M = Mg(II), Zn(II), Cu(II), Fe(II), Co(II), 2Ag(I)) on potassium bromide (chloride) discs have been determined in the 400–3800 cm^{-1} region.(11) Thus the spectral characteristics of both the α- and β-modifications of each phthalocyanine are practically independent of the type of central atom. Several bands are observed whose frequencies are dependent on the chemical identity of the central metal atom in MPc, presenting the possibility of identification of metallic phthalocyanines from their IR spectra. These findings were later confirmed by comparison of the spectra of PcSn, PcPb in the 286–5000 cm^{-1} range.(12)

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* The β-modification is most stable and its purple-reflexed needles are obtained by recrystallizing or vacuum-subliming crude phthalocyanines. The metastable α-modification is formed on continuous grinding or reprecipitation from concentrated sulphuric acid solution (into excess water) of β-needles.

(8) The present work.

(9) C. G. CANNON and G. B. B. M. SUTHERLAND, *Spectrochim. Acta.* **4,** 373 (1951).

(10) A. A. EBERT and H. B. GOTTLIEB, *J. Amer. Chem. Soc.* **74,** 2806 (1952).

(11) A. N. SIDOROV and I. P. KOTLYAR, *Opt. Spectr.* **11,** 92 (1961).

(12) W. J. KROENKE and M. E. KENNEY, *Inorg. Chem.* **3,** 696 (1963).

EXPERIMENTAL

Materials

O-cyanobenzamide was prepared by dehydration of *o*-phthalic acid diamide with acetic anhydride(13) and unrecrystallized material (M.R. 168°–172°C; lit. 173°C) was used in metal-phthalocyanine syntheses. 1-chloronaphthalene was twice vacuum-fractionated to constant refractive index. Platinum-group metal chlorides and osmium tetroxide (Johnson, Matthey Co. Ltd) were used without further purification.

Apparatus, assays

Visible absorption spectra in the region 550–750 mμ were determined using 1-cm silica cells on the Unicam SP.600 instrument. Magnetic measurements at room temperature only were carried out with a Gouy apparatus.

Microanalyses were carried out by Alfred Bernhardt, Max Planck Institute, Mülheim, Ruhr, Germany.

Syntheses

Phthalocyanine(2) ($C_{32}H_{18}N_8$ or PcH_2), (*phthalocyanino*) *platinum*(*II*)(2) PtPc and (*monochlorophthalocyanino*) *palladium*(*II*)(2) PdPcCl were synthesized and purified by standard methods. PdPcCl, unlike PtPc, does not sublime in nitrogen at dull red-heat and reduced pressure (ca. 0·5–1·0 mm). The crude product, under these conditions, gave a small amount of blue sublimate whose composition corresponded to (*phthalocyanino*) *palladium* (*II*), PdPc (Found: C, 62·1; H, 2·0; N, 19·3; Pd, 17·4%; Pd($C_{32}H_{16}N_8$) requires C, 62·0; H, 2·6; N, 18·1; Pd, 17·2%).

VISIBLE ABSORPTION SPECTRA IN 1-*Chloronaphthalene*; *Microassays*

Compound	$C_{32}H_{18}N_8$		($C_{32}H_{16}N_8$) Pt		($C_{32}H_{15}ClN_8$) Pd	
Absorption properties Bands	λ_{max} mμ	log ϵ	λ_{max} mμ	log ϵ	λ_{max} mμ	log ϵ
a_1	698	5·08				
a_2			646	5·27	648	5·36
b	664	5·04	624	4·65	624	4·54
c	640	4·50	586	4·55	587	4·61
d	602	4·32				

	Analyses									
Elements	C	H	N	C	H	N	C	H	N	Pd
Found (%)	74·1	3·7	21·8	54·5	2·2	15·8	59·7	2·5	16·8	16·0
Required (%)	74·6	3·5	21·8	54·3	2·2	15·8	58·8	2·3	17·2	16·3

The platinum-group metal phthalocyanines are synthesized in good yield (ca. 80%) by heating the metal salt and excess 1,2-dicyanobenzene (or *o*-cyanobenzamide in some cases) at 280°–300°C for 2–5 hr. The reaction products of Rh, Ir, Ru, Os chlorides with 1,2-dicyanobenzene (and/or *o*-cyanobenzamide) could not be recrystallized. Therefore, optimum reaction conditions and purificative methods were carefully determined to obtain the reproducible products described below.

(*Phthalocyanino*) *chlororuthenium*(*III*) *monophthalonitrilate*. $Pc{\cdot}RuCl{\cdot}C_6H_4(CN)_2$. (where phthalonitrile = 1,2-dicyanobenzene). $RuCl_3{\cdot}3H_2O$ (0·014 mole) and excess 1,2-dicyanobenzene (0·2 mole) were mechanically stirred together under nitrogen and their temperature was rapidly raised to and maintained at 290°C for 2–3 hr. In this way the yield of PcH_2 was minimized and that of the metal phthalocyanine greatest. Excess 1,2-dicyanobenzene and other impurities were removed

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(13) ASCHAN, *Ber.* **19**, 1399 (1886).

by prolonged Soxhlet extraction (6–12 hr) with acetone. Microanalysis of the product, a deep blue-green powder, indicated the stoichiometry $PcRuCl{\cdot}C_6H_4(CN)_2$ (Found: C, 57·1; H, 2·6; N, 16·2; Cl, 6·6; Ru, 12·7%; $(C_{32}H_{16}H_8)\ RuCl{\cdot}(C_8H_4N_2)$ requires C, 61·8; H, 2·6; N, 18·0; Cl, 4·5; Ru, 13·0%). Repetition of this preparation under varying conditions e.g. temperature, gave lower yields of products of the same composition.

Spectra in 1-chloronaphthalene solutions have an intense band at 647–8 mμ and acetone solutions an intense band in the range 625–638 mμ. The exact position of the latter depended on the particular purificative treatment of the sample. Magnetic properties: $\mu^{20}_{\text{effective}} = 1{\cdot}5$ B.M.

(Phthalocyanino) chlororuthenium(III), mono-cyanobenzamide. $PcRuCl{\cdot}C_6H_4(CN)(CONH_2)$. A similar but better characterized adduct is obtained by the reaction of excess *o*-cyanobenzamide with $RuCl_3{\cdot}aq.$ under the described conditions. (Found: C, 60·0; H, 2·8; N, 17·1; Cl, 5·3; Ru, 12·4%; $(C_{32}H_{16}N_8)\ RuCl{\cdot}(C_8H_6N_2O)$ requires C, 60·4; H, 2·8; N, 17·6; Cl, 4·5; Ru, 12·7%). Excess *o*-cyanobenzamide was best removed from the crude product by treatment with boiling aqueous/ethanolic potassium hydroxide. Microanalysis showed, however, that partial removal of the "solvating" *o*-cyanobenzamide was achieved by this method i.e. C,N figures decreased and Ru,Cl ones increased.

(Phthalocyanino) ruthenium(II) bi-anilinate. $PcRu{\cdot}2C_6H_5NH_2$. The adducts $PcRuCl{\cdot}C_6H_4(CN)_2$, $PcRuCl{\cdot}C_6H_4(CN)(CONH_2)$ were Soxhlet extracted with boiling aniline and *(phthalocyanino)* ruthenium(II). hexa-anilinate, $PcRu{\cdot}6C_6H_5NH_2$,(5) precipitated with ether from the deep blue-green aniline solution after concentration. (Found: C, 67·1; H, 3·6; N, 16·7%; $(C_{32}H_{16}N_8)$ $Ru{\cdot}6\ C_6H_5NH_2$ requires C, 69·5; H, 5·0; N, 16·7%). Prolonged Soxhlet extraction of these adducts with large volumes of methyl cyanide failed to produce PcRu(5) but only completed purification of the hexa-anilinate. The latter was recrystallized from a fresh portion of aniline giving purple-needles. These were dried at 100°C and 0·01 mm pressure for 3 hr to give the bi-anilinate (Found: C, 65·9; H, 4·1; N, 17·3; Ru, 12·7%; $(C_{32}H_{16}N_8)\ Ru{\cdot}2\ C_6H_5NH_2$ requires C, 65·9; H, 3·8; N, 17·5; Ru, 12·7%). Both the bi- and hexa-anilinates have intense absorption maxima at 631–632 mμ in benzene solution ($PcRu{\cdot}6C_6H_5NH_2$, $\lambda_{\max} = 632$ mμ in benzene(5)).

(Phthalocyanino) chlororuthenium(III), pyridine adduct. Crude $PcRuCl{\cdot}C_6H_4(CN)_2$ was Soxhlet extracted with boiling pyridine for 5 hr. On addition of ether to the resulting pyridine solution, the product separated as a chlorine-containing deep blue-green solid (Found: Ru, 9·9; C, 62·9%; $PcRuCl{\cdot}4C_5H_5N$ requires Ru, 9·7; C, 65·5%; $PcRuCl{\cdot}5C_5H_5N$ requires Ru, 10·5; C, 64·7%). The stoichiometry indicated is $PcRuCl{\cdot}nC_5H_5N$ ($n = 4$ to 5).

(Phthalocyanino) chloro-osmium(III) monophthalonitrilate. $PcOsCl{\cdot}C_6H_4(CN)_2$. $(NH_4)_2(OsCl_6)$ (0·014 mole) and excess 1,2-dicyanobenzene (0·16 mole)(3) were heated at 360°C for 5–7 hr; hydrogen chloride was evolved. Purification of the crude product involved washing with hot benzene and alcohol and prolonged Soxhlet extraction (25 hr) with acetone. The dry product was a dark-blue powder (Found: C, 54·6; H, 2·6; N, 16·1; Cl, 4·8*; Os, 22·8%; $(C_{32}H_{16}N_8)\ OsCl{\cdot}(C_8H_4N_2)$ requires C, 55·4; H, 1·7; N, 16·2; Cl, 4·1; Os, 22·0%). Spectra in 1-chloronaphthalene and acetone solutions have intense bands at 625 and 608 ± 2 mμ respectively. Magnetic properties: $\mu^{20}_{\text{effective}} = 1{\cdot}1$ B.M.

(Phthalocyanino) dioxo-osmium(VI) monophthalonitrilate. $PcOsO_2{\cdot}C_6H_4(CN)_2$. The synthesis(6) was carried out essentially under the conditions described above for that of $PcRuCl{\cdot}C_6H_4(CN)_2$ except that OsO_4 (0·014 mole) was carefully added to the stirred, molten 1,2-dicyanobenzene (0·115 mole) at ca. 180°C. The melt temperature was quickly raised to 290°C and maintained for 4 hr. The product, after prolonged Soxhlet extraction (25 hr) with acetone, was a dark-blue solid (Found: C, 54·6; H, 3·5; N, 16·0; O, 3·6; Os, 21·9%; $(C_{32}H_{16}N_8)\ OsO_2\ (C_8H_4N_2)$ requires C, 54·6; H, 2·3; N, 16·2; O, 3·7; Os, 22·0%).

Spectra in 1-chloronaphthalene and acetone solutions have intense absorption bands at 613 ± 2 and 610–613 mμ respectively. Magnetic properties: $\mu^{20}_{\text{effec.}}$ ca. 1·4 B.M.

(Phthalocyanino) dioxo-osmium(VI) tri-anilinate. $PcOsO_2{\cdot}3C_6H_5NH_2$. $PcOsO_2{\cdot}C_6H_4(CN)_2$ (0·013 mole) was refluxed with aniline (0·088 mole) for 3 hr and the solution filtered whilst hot. Ether was added to the latter when cool and the product separated. Another reprecipitation from aniline (0·033 mole) with ether gave a blue-black powder. Residual solvent was removed from this solid by

* Chlorine content determined by sodium carbonate sintering of complex in which the Os present is reduced to the metal and readily separated from soluble chloride by water leaching. This minimizes OsO_4 interference in assay.

heating it at ca. 135°C for 2 hr at 0·005–0·01 mm pressure in the presence of P_4O_{10}. (Found; C, 58·5; H, 3·6; N, 15·3; O, 3·0%; $(C_{32}H_{16}N_8)\ OsO_2{\cdot}3C_6H_5NH_2$ requires C, 59·0; H, 3·6; N, 15·2; O, 3·2%).

Solutions in 1-chloronaphthalene and acetone have intense absorption bands at 618 and 613 mμ respectively.

(Monochlorophthalocyanino)chloroiridium(III)mono-phthalonitrilate. $PcCl{\cdot}IrCl{\cdot}C_6H_4(CN)_2$.

The product of heating $IrCl_3{\cdot}3H_2O$ (0·03 mole) and excess 1,2-dicyanobenzene (0·39 mole) at 280°C for 2 hr was a deep-blue solid containing ca. 16% Ir and chlorine. Prolonged Soxhlet extraction (36 hr) with acetone completed the purification (Found: C, 51·8; H, 2·6; N, 16·0; Cl, 8·0; Ir, 20·9%; $(C_{32}H_{15}ClN_8){\cdot}IrCl(C_8H_4N_2)$ requires C, 53·1; H, 2·1; N, 15·5; Cl, 7·9; Ir, 21·4%). Solutions in acetone show absorption maxima at 581, 638 mμ.

(Phthalocyanino) iridium(II) hexa-anilinate. $PcIr{\cdot}6C_6H_5NH_2$. $IrCl_3{\cdot}3H_2O$ (0·024 mole) was heated with excess *o*-cyanobenzamide (0·31 mole) at 270°–290°C for 3 hr. The powdered product was Soxhlet extracted with glacial acetic acid (6 hr) and ethanol (1 hr). The resulting deep-blue-green solid contained 19·5% Ir and chlorine ($PcIrCl{\cdot}C_6H_4(CN)(CONH_2)$ requires 21·8% Ir) and was prepared in excellent yield.

The crude $PcIrCl{\cdot}C_6H_4(CN)(CONH_2)$ (15 g) was Soxhlet extracted with aniline (150 ml) for 7 hr and the deep blue-green adduct precipitated from the aniline extract, after concentration, with ether. Yield: 5 g (Found: C, 61·9%; H, 3·7%; N, 15·4%; Ir, 15·7%; negligible chlorine; $PcIr{\cdot}6C_6H_5NH_2$ requires C, 63·6; H, 4·6; N, 15·5; Ir, 15·2%).

(Phthalocyanino) chlororhodium(III). PcRhCl. $RhCl_3{\cdot}3H_2O$ (0·014 mole) and *o*-cyanobenzamide (0·12 mole) were heated together at 280°C for 4 hr. Water and then hydrogen chloride were evolved from the molten reaction mixture. The purplish product was successively Soxhlet extracted with ethanol (1 hr), benzene (1 hr) and acetone (36 hr). The blue-green residue was dried at 110°C after washing with ether. Yield: 90% (Found: C, 61·0; H, 2·5; N, 17·5; Cl, 4·8; Rh, 15·7%; $(C_{32}H_{16}N_8)$ RhCl requires C, 59·0; H, 2·5; N, 17·2; Cl, 5·5; Rh, 16·0%). This product probably contains traces of *o*-cyanobenzamide: vide high C, N and low Rh, Cl figures. Solutions in acetone show absorption maxima at 584, 645 mμ.

RESULTS

The IR absorption frequencies of the platinum-group metal phthalocyanines described in this work are reported in Table 1. Spectra in the range 220–680 cm^{-1} were obtained on Nujol suspensions held between thin polythene sheets on a GRUBB–PARSONS DM4 (double beam) instrument at ca. 0% relative humidity. Those in the range 650–5000 cm^{-1} were obtained with the sample pressed into potassium bromide (or chloride) discs on the Unicam SP. 200 instrument. Typical, complete spectra of PcH_2, PdPcCl, PtPc, PcRhCl, $PcOsCl{\cdot}C_6H_4(CN)_2$ are shown in Fig. 1.

Satisfactory spectra in the range 220–680 cm^{-1} have only been obtained for PcH_2, PtPc, PdPcCl, $PcCl{\cdot}IrCl{\cdot}C_6H_4(CN)_2$, $PcOsCl{\cdot}C_6H_4(CN)_2$. The clearest spectra in this region were obtained for those phthalocyanines which had been purified by recrystallization, i.e. PcH_2, PtPc, PdPcCl. On the other hand, the spectra of PcRhCl, $PcRuCl{\cdot}C_6H_4(CN)_2$, $PcOsO_2{\cdot}C_6H_4(CN)_2$ and $PcRu{\cdot}2C_6H_5NH_2$ showed no identifiable absorption maxima (see Fig. 1). Examination of the KBr discs of the latter compounds between 400–700 cm^{-1} also revealed no characteristic absorption maxima. Hence it seems that radical improvements in the "far-IR" sampling techniques are necessary to obtain clear spectra of such compounds.

DISCUSSION

220–680 cm^{-1} *region*

No assignments are made but it is readily seen that the spectra of the platinum-group metal phthalocyanines are more complex than that of PcH_2 (Fig. 1 and Table 1).

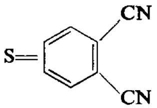
Notes: S=


Table 1.—Ir spectra of P.M. phthalocyanines. (220–5000 cm^{-1}) All wavenumbers correct to ±2 cm^{-1}

Compound	PcH_2		PtPc		PdPcCl		PcRhCl		PcCl·IrCl·S		PcRuCl·S		$PcRu{\cdot}2C_6H_5NH_2$		PsOsCl·S		$PcOsO_2{\cdot}S$	
Phase 220–680 cm^{-1} 650–5000 cm^{-1}	Solid between polythene KBr disc		Solid between polythene KBr disc		Nujol Mull/CsI KBr disc		KBr disc		Solid between polythene KBr disc		KCl disc		KBr disc		Solid between polythene KBr disc		KBr disc	
Line No.	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity	λ cm^{-1}	Intensity
1	227	ms	229	mw	223	m			228	ms					226	m		
2			246	wm	243	wm			241	w					243	w		
3			250	wm	252	wm									252	w		
4	258	ms							256	m					258	m		
5					265	w												
6			275	wm	277 280	wm			275	m					270	wm		
7			287	w	288	w			287	w					285	w		
8	301	w	299	w	301	wm			299	w					299	w		
9			306	w	328	m												
10	340	wm	348	w	351 363	vs m									348	w		
11			375	ms	373	wm									371	wm		
12	397	w							393	w								
13	433 441	s m	433	m	433	m			439	s					439	s		
14	487	m							483	w								
15			505	wm	510	w			510	w								
16			535	m	532	w			535	m								
17			565	w	571	wm			568	w								
18	610	s																
19									633	wm								
20	671	m	662	m	662	m			662	m					662	m		
21	678	w											690	ms				
22	708	ms																

23	729	vs	726	s	724	s	732	s	734	s	735	s	735	s	730	s	730	s
24	761	wm	756	m	756	wm	756	s	757	s	752	m	754	s	754	s	755	s
25			772	wm	771	w	778	m	766	wm	775	w	778	ms	772	ms	776	ms
26			816	vw			835	w	861	w								
27	874	ms	872	w	876	w	880	w	877	w	870	vw	877	w	871	w	877	w
28			918	m	918	ms	914	ms	917	m	909	m	915	m	912	m	911	m
29	950	w	947	vw	955	w	952	w			952	w	950	w	951	w		
30	1009	vs	1008	w	1011	w	1006	w	1013	wm	1010	m	1008	w				
31	1044	w																
32			1076	m	1076	wm	1069	s	1072	w	1064	s	1068	ms	1069	s	1069	s
33	1095	m																
34	1119	ms	1129	s	1124	s	1127	s	1128	s	1120	s	1131	s	1129	s	1127	s
35	1160	w	1170	s	1170	m	1169	s	1173	ms	1167	m	1174	s	1172	ms	1172	ms
36	1249	w			1257	w												
37	1273	m	1289	ms	1289	m	1284	s	1290	ms	1289	m	1289	s	1287	ms	1290	ms
38	1301	w																
39	1320	ms																
40	1332	ms	1327	ms	1330	ms	1328	s	1331	ms	1326	s	1326	s	1329	s	1332	ms
41	1386	w	1354	wm	1354	w	1351	w	1367	ms							1370	ms
42	1436	m	1422	ms	1420	m	1417	s	1422	m	1412	ms	1415	s	1410	ms	1416	ms
43	1459	w	1466	w	1464	w	1462	w	(1439)	wm	1443	m			1452	w		
44	1476	w	1481	w	1481	w			1464 ± 4	w								
45	1503	m	1515	ms	1511	m	1504	s	1505	w	1486	s	1493	s	1489	ms	1489	ms
46									1530	s					1525	w	1532	ms
47							1587	w	1582	wm			1582	w				
48	1620	m	1614	ms	1614	ms	1612	s	1620	w	1608	w	1605	ms	1616	ms	1616	ms
49											1639	s						
50									1725	w	1709	wm					1727	s
51							2250	vw(wide)	2220	wm	2230	w					2215	wm
52													2585	w				
53			2945	vw	2955	w			2955	w			2940	wm			2960	vw
54			3060	w	3080	wm	3075	w	3100	vw			3063	wm			3080	w
Predominant Polymorph	β		α		α		β		β		α		β		β		β	

650–5000 cm^{-1} *region*

A close comparison of these spectra with those of the α- and β-forms of PcH_2, MPc (M = Mg, Zn, Cu, Fe, Co, Ni) enable the predominant polymorph in each compound to be identified. The platinum-group metal phthalocyanines purifiable by direct recrystallisation are mainly in the α-modification.* The others, whose purification involved prolonged heating during solvent extraction, exist mainly in the stabler β-modification.

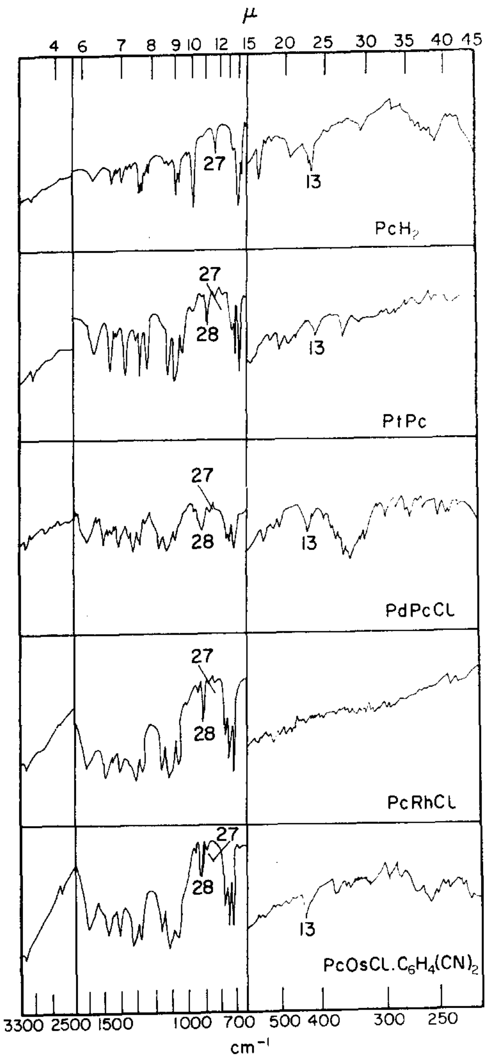


FIG. 1.—Typical infra-red spectra of phthalocyanine and some of its platinum-group metal derivatives. The ranges represented above lie between 220–1700, 2000–3300 cm^{-1} respectively. For the sake of clarity, the background traces of the Nujol mulling agent in the 220–650 cm^{-1} region are not shown.

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* See footnote page 4 and reference 11.

Table 2 compares the bands reported$^{(11)}$ to be relatively metal-sensitive in Fe, Co, Ni phthalocyanines with those of the platinum-group metals. Thus the Ru, Rh, Pd and Os, Ir, Pt triads follow the same trend as that of Fe, Co, Ni, the band frequency increasing somewhat with atomic number and weight. Lines No. 28, 32, 42 (see Tables 1 and 2) indicate an increase in frequency in the sequence Os, Ru $<$ Rh $<$ Ir $\leqslant$ Pt $\leqslant$ Pd. Lines No. 32, 42 could be associated with medium intensity bands at 1095, 1436 cm^{-1} of PcH_2 but lowered in frequency by between 14 and 26 cm^{-1}. Such bands occur in the heterocyclic ring deformation and C=N/C=C stretching vibration regions. The medium intensity band at 874 cm^{-1} of PcH_2 may be related to line 28 and is more metal-sensitive, varying in frequency from 881 cm^{-1} for PbPc$^{(12)}$ to 918 cm^{-1} for PtPc, PdPcCl.$^{(8)}$ The PcH_2 band may be a ring vibration of the substituted pyrrole units, having too low a frequency for heterocyclic NH deformations e.g. as in substituted indoles.$^{(14)}$ Alternatively, the authors tentatively suggest the 914 cm^{-1} band to be a rocking vibration of the metal–phthalocyanine nucleus. This follows from its unambiguous position, metal-sensitivity and intensity—the latter being too high for an overtone of the X-sensitive bands at 433–439 cm^{-1} (line 13). The rocking vibration would be directly related to the strength of the metal–nitrogen bonds in these phthalocyanine chelates. A similar relationship has been demonstrated for the tetraphenylporphine chelates$^{(15)}$ of Cu(II), Co(II), Ni(II), Pd(II), Pt(II).

TABLE 2.—RELATION BETWEEN IR ABSORPTION FREQUENCIES OF METAL PHTHALOCYANINES AND CENTRAL METAL ATOM

	Phthalocyanines and their Crystalline phase, α and/or β								
Line no. (Table 1)	Ru α* and β λ_d	Rh β λ_d	Pd α λ_d	Os β λ_d	Ir β λ_d	Pt α λ_d	Fe α and β λ_d	Co α and β λ_d	Ni α and β λ_d
28	910	914	918	911	917	918	910	915	917
32	1064*	1069	1076	1069	1072	1076	1072	1075	1078
37	1288	1284	1289	1287	1290	1289	1290	1291	1291
42	1412	1417	1420	1410	1422	1422	1422	1428	1429
43	1443	1462	1464	1452	1464	1466	1468	1471	1472
45	1487	1504	1511	1489	1505	1515	1484	1487	1493
48	1607*	1612	1614	1616	1620	1614	1592	1597	1599

λ_d = Absorption maximum in the halide disc media, given to ± 1 cm^{-1}

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(14) B. WITKOP and J. B. PATRICK, *J. Amer. Chem. Soc.* **73**, 713, 1558 (1951).

(15) D. W. THOMAS and A. E. MARTELL, *J. Amer. Chem. Soc.* **81**, 5111 (1959).