in which no ordering of the vacancies could be detected. Although the fully oxidized $Cs_3M_2Cl_9$ phases for 3d elements other than scandium have a different structure, it would not be particularly surprising to find that the $CsMCl_3$ salts for at least titanium and vanadium may be significantly substoichiometric on the B sites. Evidence for the presence of voids and mixed oxidation states on the B sites in perovskite-related ABX_3 phases has been obtained by McPherson and coworkers[24] in systems containing small amounts of paramagnetic gadolinium(III) or chromium(III) cations in, for example, a $CsMgCl_3$ host. In this case the trivalent B ions occur in pairs around a cation vacancy, a reasonable situation based on local lattice interactions. At least in the scandium system such effects do not take place with long-range order until somewhat more than 30% of the sites are vacant. Work is continuing by using EPR and NMR techniques as more sensitive probes of short-range order: at the present time NMR data do not appear to provide any particular clarification of the reduction process.

Complete occupation of the octahedral sites at the limiting composition $CsScCl_3$ is achieved in a single-phase product with only small changes in lattice constants. This scandium salt completes the series for dipositive 3d elements, as this structure is already known for Ni, Co, Fe, V, and Ti and, in distorted form, for Cu, Mn, and Cr.[4,5] The packing of the Cs + 3Cl layers so dominates these structures that the metal–metal distances along the chains parallel to c are all 3.01 or 3.02 Å for elements from Sc through Co while the a parameters show a 1.7% decrease over the same range. The fully reduced $CsScCl_3$ is isoelectronic and isostructural with the sulfide analogue $BaVS_3$,[25] a metallic conductor which has been the subject of recent interest.[18,26]

Acknowledgment. We continue to be indebted to Professor Robert A. Jacobson for the use of the diffractometer facilities and to Professor Karl Gschneidner and his group for the availability of both the high-purity scandium metal and the tantalum welding equipment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.

Registry No. $Cs_3Sc_2Cl_9$, 12272-71-8; $CsScCl_3$, 65545-44-0.

Supplementary Material Available: A listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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[24] G. L. McPherson and L. M. Henling, *Phys. Rev. B*, **16**, 1889 (1977).

[25] R. A. Gardner, M. Vlasse, and A. Wold, *Acta Crystallogr., Sect. B*, **25**, 781 (1969).

[26] M. Takano, H. Kosugi, N. Nakanishi, M. Shimada, T. Wada, and M. Koizumi, *J. Phys. Soc. Jpn.*, **43**, 1101 (1977).

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Synthesis and Structure of a New Class of Metallophthalocyanines: Carbonyl(phthalocyanato)(pyridine or tetrahydrofuran)ruthenium(II) and Carbonyl(phthalocyanato)(pyridine or tetrahydrofuran)osmium(II)

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During our synthesis of (phthalocyanato)ruthenium(II) and (phthalocyanato)osmium(II) complexes reported by Berizin and Sennikova and by Krueger and Kenny, we observed a remarkable solubility of these complexes in common organic solvents. The solubility of these complexes enabled us to isolate several pure reported and new phthalocyanine complexes. Among the complexes we studied, carbonyl(phthalocyanato)(pyridine)ruthenium(II) [PcRu(CO)(py)], carbonyl(phthalocyanato)(pyridine)osmium(II) [PcOs(CO)(py)], and carbonyl(phthalocyanato)(tetrahydrofuran)ruthenium(II) [PcRu(CO)(THF)] were isolated in pure form. They are among the first reported metallophthalocyanines with a carbonyl as one of their axial ligands. Furthermore, several new ways of synthesizing these complexes in quantitative yields have been established. The structure of PcOs(CO)(py) is elucidated by the X-ray diffraction analysis. The osmium ion is octahedrally coordinated with the carbonyl and pyridine groups axially coordinated. The pyridine ring is tilted slightly with respect to the perpendicular to the phthalocyanine ring. The interplanar angle is 98.6°. Interesting comparisons may be made between PcOs(CO)(py) and related porphyrin complexes.

Phthalocyanine and metallophthalocyanines demonstrate significant electrical and photo properties,[1,2] e.g., semiconductivity, photoconductivity, photochemical reactivity, luminescence, and fluorescence, which are relevant to the current world problem of conversion and production of energy. The number of publications per year on chemistry of phthalocyanines and metallophthalocyanines has tripled during the past decade. During 1977, nearly 700 papers and patents were published. In spite of the increasing interest in this area and the near completion of the synthesis of all metal ions having the normal classic configuration, basic phthalocyanine chemistry has lacked the advantage of any dynamic or extraordinary progress. Many metalloporphyrins[3] have been made and studied extensively, and a large body of coordination chemistry of these complexes has been developed, while the coordination chemistry of metallophthalocyanines has been poorly developed. This contrast is mainly due to the significantly lower solubility of metallophthalocyanines and has led to the presumption that the development of coordination chemistry of phthalocyanines is difficult in general.

During our synthesis of (phthalocyanato)ruthenium(II) and (phthalocyanato)osmium(II) complexes reported by Berizin and Sennikova[4,5] and by Krueger and Kenny,[6a] we have found

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[1] Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.

[2] Moser, F. H.; Thomas, A. L. *ACS Monogr.* **1963**, *No. 157*.

[3] Smith, K. M., Ed., "Porphyrins and Metalloporphyrins"; Elsevier: Amsterdam, 1975.

0020-1669/80/1319-0134$01.00/0 © 1980 American Chemical Society

a remarkable solubility of these complexes in common organic solvents. The solubility of these complexes enabled us to isolate several pure reported and new phthalocyanine complexes. Among the complexes we studied, carbonyl(phthalocyanato)(pyridine)ruthenium(II) [PcRu(CO)(py)], carbonyl(phthalocyanato)(pyridine)osmium(II) [PcOs(CO)(py)], and carbonyl(phthalocyanato)(tetrahydrofuran)ruthenium(II) [PcRu(CO)(THF)] were isolated in pure form. These compounds are among the first reported metallophthalocyanines with carbonyl as one of their axial ligands. Furthermore, several new ways of synthesizing these complexes in quantitative yields have been established. Since the completion of this work,[6c] the preparation of PcRu(CO)(L)L (L = py, 4-Me-py, 4-*t*-Bu-py) has been reported by Farrell et al.[6b] by Farrell *et al.*[6b] However, the methods of preparation described herein, which differ from their techniques, produce products in considerably higher yield. In this paper we also describe the structure of PcOs(CO)(py) as determined from an X-ray diffraction analysis. This is the first reported structure of this type of phtalocyanine complex and provides interesting comparisons with analogous porphyrin complexes.

Experimental Section

Materials. Phthalonitrile (practical) was purchased from the Eastman Kodak Co. and used without any further purifications. Ruthenium trichloride trihydrate ($RuCl_3 \cdot 3H_2O$) and osmium tetraoxide (OsO_4) were purchased from the Ventron Corp. and used without any further purifications. Ruthenium dodecacarbonyl ($Ru_3(CO)_{12}$) and osmium dodecarbonyl ($Os_3(CO)_{12}$) were purchased from Strem Chemicals and used without purification. Carbon monoxide gas (99.9%) was purchased from the Matheson Gas Co. and used without purification. Pyridine (reagent grade), tetrahydrofuran (reagent grade), methylene chloride (spectro grade), chloroform (spectro grade), and benzene (spectro grade) were used without further purification. Neutral alumina (60–100 mesh), acid alumina (80–200 mesh), and silica gel (60–200 mesh) were purchased from the Fisher Scientific Co.

Physical Measurements. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Visible spectra were measured with a Beckman spectrophotometer, Model 24. Infrared spectra were measured with a Beckman infrared spectrophotometer, Model IR-8.

Isolation of PcRu(CO)(THF) from the Products of the Reaction of $RuCl_3 \cdot 3H_2O$ with Phthalonitrile. $RuCl_3 \cdot 3H_2O$ (1.00 g, 3.8 mmol) was heated with excess phthalonitrile (8.00 g, 62.5 mmol) at 250 °C for 4 h. After the resulting product was washed with methanol several times, unreacted phthalonitrile was removed by sublimation at 150 °C under vacuum. The blue-black residue (4.1 g), which was left at the bottom of the sublimator, was dissolved in aniline (10 mL), and metal-free phthalocyanine was removed from the solution by filtration. The aniline solution was poured into benzene (1.0 L) with stirring. A black precipitate (0.8 g) was separated by filtration from the benzene solution. The solution was then concentrated and dried under vacuum at 100 °C until aniline in the solution was removed. The dried residue (3.5 g) was dissolved in benzene (30 mL), and then the solution was chromatographed over silica gel with benzene. Meanwhile, benzene was replaced by chloroform, and a light blue band, which was most intense, was separated from the dark blue band. The light blue eluate was condensed and chromatographed over neutral alumina with chloroform. Another bright blue band followed the original blue band when tetrahydrofuran was added to chloroform. The second blue eluate was condensed and dried. Fine needle crystals (120 mg) with a typical phthalocyanine appearance of red reflection and blue transmission were obtained. The visible spectrum of this compound shows maxima at 642 and 581 nm (in chloroform). The infrared spectrum has an intense peak at 1960 cm^{-1}.

Preparation of PcRu(CO)(py) from $RuCl_3 \cdot 3H_2O$ and Phthalonitrile in Carbon Monoxide. $RuCl_3 \cdot 3H_2O$ (100 mg, 0.38 mmol) was heated in molten phthalonitrile (500 mg, 1.9 mmol) under carbon monoxide atmosphere at 250 °C for 4 h. After the product was cooled to room temperature, pyridine (5 mL) was added to the cake. The mixture was again heated to the boiling temperature of pyridine for 1 h. The pyridine solution of the resulting product was cooled to room temperature, and then pyridine was removed first by distillation. Excess amounts of phthalonitrile were removed by sublimation at 150 °C under vacuum. The blue residue (265 mg) was dissolved in methylene chloride (15 mL), and the solution was chromatographed over neutral alumina with methylene chloride. The first blue band was followed by a second blue band when methylene chloride was replaced with chloroform. The second blue eluate, which was present in large quantity, was condensed and dried at 100 °C under vacuum. A fine blue powder (230 mg) with red reflection (PcRu(CO)(py)) was obtained (84% yield). Anal. Calcd for PcRu(CO)(py): Ru, 14.02; N, 17.49. Found: Ru, 13.97; N, 17.35. The visible spectrum shows maxima at 624 and 581 nm (in chloroform). The infrared spectrum shows an intense peak at 1965 cm^{-1}.

Preparation of PcRu(CO)(py) from $Ru_3(CO)_{12}$ and Phthalonitrile. $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) was added to molten phthalonitrile (500 mg, 1.9 mmol) in air and heated at 250 °C for 4 h. The product was heated with pyridine (5 mL) at 150 °C for 1 h. Pyridine and unreacted phthalonitrile were removed, and the residue was dissolved in methylene chloride. Chromatography of the solution over neutral alumina gave a single blue band with chloroform. The chloroform eluate was condensed and dried. The blue powder (PcRu(CO)(py)) with red reflection weighed 315 mg (91% yield).

Isolation of PcOs(CO)(THF) from the Products of the Reaction of OsO_4 with Phthalonitrile. OsO_4 (1.0 g, 3.9 mmol) was added to molten phthalonitrile (6.0 g, 46.8 mmol) in a 50-mL flask equipped with a condenser. The mixture was kept at 250 °C for 4 h. The excess phthalonitrile was removed from the product by sublimation. The residue was put in an extraction thimble, and some products were extracted with tetrahydrofuran. The THF solution was condensed and dissolved in chloroform. The chloroform solution was chromatographed over acid alumina with chloroform. The first blue band was collected and condensed. The condensed residue was then chromatographed over neutral alumina with chloroform. The first blue band of the second chromatography was collected and condensed. After drying of the mixture at 100 °C under vacuum, a blue powder (PcOs(CO)(THF)) was obtained (115 mg, 3.7% yield). Anal. Calcd for PcOs(CO)(THF): Os, 23.69; N, 13.96. Found: Os, 23.20; N, 14.15. The visible spectrum of the compound shows maxima at 636 and 576 nm in THF. The infrared spectrum of the compound shows an intense peak at 1930 cm^{-1}.

Preparation of PcOs(CO)(py) from OsO_4 and Phthalonitrile in Carbon Monoxide. OsO_4 (107 mg, 0.42 mmol) was added to molten phthalonitrile (500 mg, 3.9 mmol) in a 50-mL round-bottom flask equipped with a condenser under carbon monoxide stream. The mixture was kept at 250 °C for 4 h under a carbon monoxide atmosphere. The mixture was then cooled to room temperature and dissolved in pyridine (5 mL). The pyridine solution was refluxed for 1 h under a carbon monoxide atmosphere. Pyridine and phthalonitrile were removed under vacuum from the product. The resulting blue residue was dissolved in chloroform (50 mL), and metal-free phthalocyanine was removed from the chloroform solution by filtration. The chloroform solution was condensed and chromatographed over neutral alumina with chloroform. The single blue band was collected and condensed. A blue powder with red reflection (PcOs(CO)(py)) was obtained after drying (280 mg, 83% yield). Anal. Calcd for PcOs(CO)(py): Os, 23.49; N, 15.57. Found: Os, 22.96; N, 15.48. The visible spectrum of the compound shows maxima at 632 and 575 nm (in chloroform). The infrared spectrum of the compound shows an intense peak at 1930 cm^{-1}.

Preparation of PcOs(CO)(py) from $Os_3(CO)_{12}$ and Phthalonitrile. $Os_3(CO)_{12}$ (100 mg, 0.11 mmol) was added to molten phthalonitrile (500 mg, 3.9 mmol) in a 50-mL round-bottom flask. The mixture was kept at 250 °C for 4 h. Pyridine (5 mL) was added to the mixture, and the pyridine solution was refluxed for 1 h. Pyridine and excess phthalonitrile were removed from the product by distillation and sublimation. The blue residue was then dissolved in chloroform, and metal-free phthalocyanine was separated from the solution by filtration. The chloroform solution was condensed and chromatographed over

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(4) Berizin, B. D.; Sennikova, G. V. *Dokl. Akad. Nauk SSSR* **1964**, *159*, 117.

(5) Berizin, B. D.; Sennikova, G. V. *Dokl. Akad. Nauk SSSR* **1962**, *146*, 604.

(6) (a) Krueger, P. C.; Kenny, M. E. *J. Inorg. Nucl. Chem.* **1963**, *25*, 303. (b) Farrell, N. P.; Murray, A. J.; Thornback, J. R.; Dolphin, D. H.; James, B. R. *Inorg. Chim. Acta* **1978**, *28*, L 144. (c) Omiya, S. Ph.D. Disseration, Texas A&M University, April 1978.

Table I. Crystal Data for $(C_{38}H_{21}N_8)Os^a$

$a = 11.966\ (9)$ Å	fw 809.9
$b = 15.705\ (3)$ Å	$Z = 4$
$c = 17.749\ (5)$ Å	$d(\text{calcd}) = 1.721$ g cm^{-3}
$B = 107.92\ (4)°$	$\mu = 43.9$ cm^{-1} (Mo Kα radiation)
$V = 3125\ (4)$ Å^3	systematic absences $h0l$ ($h + l$ odd), $0k0$ (k odd)
	space group $P2_1/n$

[a] In this and subsequent tables the estimated standard deviation of the least significant figures is shown in parentheses.

neutral alumina with chloroform. The single blue band was collected and condensed. After drying of the mixture at 100 °C under vacuum, a blue powder with red reflection (PcOs(CO)(py)) was obtained (220 mg, 82% yield).

X-ray Study. Crystals of PcOs(CO)(py) were grown from a chloroform solution. The crystal chosen for intensity measurements was a parallelepiped bounded by {100}, {010}, and {001}. The dimensions were 0.20 × 0.20 × 0.09 mm in the directions of *a*, *b*, and *c*, respectively. It was mounted in a capillary[7] at an arbitrary orientation but with *a* approximately parallel to the spindle axis.

Crystal data are listed in Table I. An Enraf-Nonius CAD-4 computer-controlled diffractometer was used. The radiation (Mo Kα, λ 0.71069 Å) was monochromatized by pyrolitic graphite. The instrument centered the crystal automatically. The setting angles for 25 reflections, measured at $+2\theta$ and -2θ, were used to index the cell and then were refined to give an orientation matrix, cell constants, and a Niggli matrix[8] which indicated that the system was monoclinic.[9] The systematic absences uniquely determined the space group.

The diffracted intensities were collected by using the θ–2θ scan technique. Scan speeds, which were determined by a rapid preliminary scan, ranged from 0.28 to 3.35°/min depending on the intensity. Very weak reflections were measured at the maximum rate. The scan range for each reflection was equal to $(0.90 + 0.35 \tan \theta)°$. Other experimental conditions are described elsewhere.[10] No evidence of crystal decomposition or machine instability was noted.

Independent reflections (4596) were measured out to a sin θ value of 0.54 or 22.5° in θ. Of these, 2820 had a net intensity greater than $2\sigma_I$ and were used in analysis. The standard deviation σ_I was defined in terms of the statistical variances of the counts as $\sigma_I^2 = \sigma_{I(\text{count})}^2 + (0.02I)^2\sigma_{I(\text{count})}$ is the variance determined solely from counting statistics. Structure factors were calculated in the usual way, including correction for partial polarization of the incident beam due to the use of a monochromator.

Determination and Refinement of the Structure. Because there are four molecules in the unit cell of space group $P2_1/n$, all atoms lie in general positions. The position of the osmium atom was found from an unsharpened Patterson synthesis. The rest of the 49 nonhydrogen atoms were found from a series of difference syntheses. Least-squares refinement using full-matrix methods was carried out minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. Initially isotropic temperature factors were used, but in the final refinements all nonhydrogen atoms were varied by assuming anisotropic thermal motion. The positions of 18 of the 21 hydrogen atoms could be found from ΔF maps. However, refinement of the hydrogen atom parameters led to chemically unreasonable bond lengths and angles. Hence the positions of all the hydrogen atoms were calculated (C–H = 0.95 Å) and their contributions included in the structure factor calculations, assuming an isotropic temperature factor, B, of 4.0 Å^2. The hydrogen atom parameters were not refined. The refinement converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.031$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.035$.

A correction for anomalous dispersion was made for all nonhydrogen atoms.[11] Scattering factors were from ref 12. The osmium atom was assumed to be in the zero ionization state. No evidence of secondary extinction was found.

Attempts to apply absorption corrections were made. Transmission coefficients, calculated by using a Gaussian integration method (6 × 4 × 6 grid), varied from 0.43 to 0.68 with most being about 0.6. The R factors increased substantially ($R = 0.049$, $R_w = 0.056$) when refinements were attempted by using the corrected data. No improvement was noted in the standard deviations. It was concluded that the errors introduced in applying the corrections to a relatively small crystal enclosed in a capillary were larger than those introduced by ignoring absorption effects. Thus, the final refinements were carried out on uncorrected data.

In the last cycle of refinement all shifts on positional and thermal parameters were less than 1 standard deviation, with the largest shift being 0.37 standard deviation. The final value of the standard deviation of an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, was 0.944 for $N_o = 2820$ reflections and $N_v = 442$ parameters.

There were two peaks of about 1.5 e/Å^3 in the final difference Fourier. These were quite close to the osmium atom. Neither they nor any of the other peaks were considered physically significant.

Most calculations were performed on a PDP 11/40 computer using the Enraf-Nonius structure determination package (SDP). Johnson's ORTEP,[13] some molecular geometry calculations (using XANADU by Roberts and Sheldrick), and local programs were run on an Amdahl 470v/6 computer. Use was made of the PDP 11/40-Vector General graphics system.[14] Data reduction was performed on the Honeywell computer at the University of Houston.

The final positional and thermal parameters are given in Table II. The final calculated positions of the hydrogen atoms are given in Table III. Tables IV and V contain the root-mean-square components of thermal displacement along the principal axis of the thermal ellipsoids and the observed and calculated structure factors respectively. Tables III–V are available as supplementary material.

Results and Discussion

The following reactions for the synthesis of (phthalocyanato)ruthenium complexes have been carefully examined, and considerable discrepancies from the reported results[4] have been found. Furthermore, a new carbonyl complex of ruthenium phthalocyanine has been isolated from the reaction products. The reaction of $RuCl_3 \cdot 3H_2O$ with phthalonitrile was reported to give $PcRu^{III}Cl$ as the major product of the reaction by Berizin and Sennikova,[4,5] as shown in the equation

$$RuCl_3(H_2O) + C_6H_4(CN)_2 \rightarrow PcRu^{III}Cl$$

The reaction of $RuCl_3 \cdot 3H_2O$ with *o*-cyanobenzoamide was reported to give $PcRu^{II}$ as its major product by Krueger and Kenny,[6a] as shown in the equation

$$RuCl_3 \cdot 3H_2O + NCC_6H_4CONH_2 \rightarrow PcRu^{II}$$

From our investigations both of these reactions have been found to give $PcRu^{II}$ as the major product and $PcRu^{III}Cl$ as the minor one.

In addition, a small quantity of $PcRu^{II}(CO)L$ (L is a solvent used for the isolation) was detected in the crude $PcRu^{II} \cdot 6C_6H_5NH_2$ according to its infrared spectrum and was isolated by column chromatography. The yield of $PcRu^{II}(CO)L$ was less than 5%. Thus, the reactions above should be expressed by the following equations:

$$RuCl_3 \cdot 3H_2O + C_6H_4(CN)_2 \rightarrow PcRu^{II} + PcRu^{III}Cl + PcRu^{II}(CO)L$$

$$RuCl_3 \cdot 3H_2O + NCC_6H_4CONH_2 \rightarrow PcRu^{II} + PcRu^{III}Cl + PcRu^{II}(CO)L$$

The yield of 5% for CO complex is rather surprising in two

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(7) Meyer, E. F., Jr. *J. Appl. Crystallogr.* **1973**, *6*, 45.

(8) Niggli, P. "Handbuch der Experimentalphysik"; Akademische Verlagsgesellschaft, 1928; p 108.

(9) Instruction Manual, CAD-4 System, Enraf-Nonius, Delft, 1977.

(10) Reisner, G. M.; Bernal, I.; Brunner, H.; Muschiol, M. *Inorg. Chem.* **1978**, *17*, 783.

(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(12) Cromer, D. T.; Waber, J. T. In "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Ed.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–101.

(13) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., revised 1965.

(14) Morimoto, C. N.; Meyer, E. F., Jr. In "Crystallographic Computing Techniques"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1976.

Table II. Fractional Coordinates and Thermal Motion Parameters Derived from the Least-Squares Refinement

ATOM	X	Y	Z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
OS	0.22473(4)	0.11171(3)	0.11752(3)	352(2)	303(2)	276(2)	-1(7)	274(3)	61(6)
N(1)	0.4585(7)	0.1150(6)	0.0454(4)	33(4)	41(5)	37(4)	0(12)	31(7)	1(11)
N(2)	0.2651(7)	0.1753(6)	0.0286(4)	31(4)	34(5)	31(4)	1(11)	27(7)	31(11)
N(3)	0.0855(7)	0.2557(5)	-0.0241(5)	42(5)	34(6)	26(5)	-5(10)	16(8)	17(9)
N(4)	0.0711(7)	0.1710(6)	0.0896(4)	32(5)	47(6)	23(4)	-5(10)	21(7)	33(9)
N(5)	-0.0051(6)	0.1119(6)	0.1914(4)	33(4)	32(5)	28(4)	8(11)	22(7)	-9(10)
N(6)	0.1925(7)	0.0575(5)	0.2143(4)	38(5)	29(5)	28(4)	-6(9)	33(7)	15(8)
N(7)	0.3804(7)	-0.0112(5)	0.2739(5)	33(5)	28(5)	43(5)	13(9)	33(8)	16(9)
N(8)	0.3844(7)	0.0620(6)	0.1521(4)	37(5)	47(6)	24(4)	-10(10)	25(8)	32(9)
C(1)	0.3667(9)	0.1631(7)	0.0084(6)	48(7)	38(7)	30(6)	-31(13)	35(10)	-21(11)
C(2)	0.3569(10)	0.2151(7)	-0.0625(6)	55(7)	27(6)	26(5)	-27(12)	37(10)	-8(10)
C(3)	0.4347(10)	0.2275(8)	-0.1073(6)	52(7)	48(8)	46(6)	-14(13)	58(10)	-4(13)
C(4)	0.3991(11)	0.2840(8)	-0.1704(6)	81(8)	56(8)	45(6)	-20(15)	86(10)	11(13)
C(5)	0.2923(11)	0.3273(8)	-0.1889(6)	96(9)	47(8)	39(6)	-50(15)	51(12)	21(13)
C(6)	0.2155(10)	0.3135(7)	-0.1460(6)	62(8)	39(7)	33(6)	-14(13)	40(11)	4(12)
C(7)	0.2483(9)	0.2568(7)	-0.0826(5)	50(7)	34(7)	22(5)	-13(12)	29(10)	1(11)
C(8)	0.1908(9)	0.2290(7)	-0.0237(6)	50(7)	30(7)	29(6)	-14(12)	36(10)	5(11)
C(9)	0.0300(9)	0.2300(7)	0.0282(6)	40(7)	30(7)	34(6)	-4(12)	18(10)	-5(11)
C(10)	-0.0855(10)	0.2601(7)	0.0268(6)	51(7)	34(7)	27(6)	10(13)	20(10)	-1(11)
C(11)	-0.1664(10)	0.3177(7)	-0.0210(6)	62(8)	41(7)	39(7)	33(14)	18(12)	24(12)
C(12)	-0.2715(10)	0.3290(8)	-0.0091(7)	46(7)	56(8)	65(8)	61(14)	20(13)	17(15)
C(13)	-0.3023(10)	0.2830(8)	0.0492(7)	51(7)	52(8)	66(8)	44(14)	40(12)	7(14)
C(14)	-0.2244(9)	0.2267(7)	0.0985(6)	34(6)	49(8)	35(6)	16(12)	25(10)	-2(12)
C(15)	-0.1166(10)	0.2150(7)	0.0874(6)	46(7)	25(6)	36(6)	10(12)	19(11)	-9(11)
C(16)	-0.0135(9)	0.1622(7)	0.1269(5)	38(6)	23(6)	23(5)	15(11)	6(10)	15(10)
C(17)	0.0883(9)	0.0669(7)	0.2311(6)	28(6)	36(7)	29(5)	-9(11)	29(9)	-5(11)
C(18)	0.1005(9)	0.0206(6)	0.3057(6)	37(6)	22(6)	28(6)	1(11)	22(9)	12(10)
C(19)	0.0226(9)	0.0057(7)	0.3493(6)	47(6)	38(7)	39(6)	-2(12)	55(9)	-5(11)
C(20)	0.0643(10)	-0.0424(7)	0.4189(6)	76(7)	39(7)	45(6)	0(13)	90(10)	15(12)
C(21)	0.1783(11)	-0.0752(7)	0.4443(6)	77(8)	46(8)	46(6)	9(14)	70(11)	29(12)
C(22)	0.2542(9)	-0.0603(7)	0.4014(6)	40(7)	50(8)	36(7)	13(13)	22(11)	4(12)
C(23)	0.2153(10)	-0.0139(7)	0.3308(5)	58(7)	26(6)	23(5)	5(12)	32(10)	14(10)
C(24)	0.2726(10)	0.0111(6)	0.2707(6)	52(7)	26(6)	24(6)	13(12)	21(10)	15(10)
C(25)	0.4314(9)	0.0105(7)	0.2180(6)	33(6)	32(7)	41(6)	-12(12)	28(10)	2(12)
C(26)	0.5508(9)	-0.0171(7)	0.2209(6)	34(6)	29(7)	40(6)	8(12)	19(10)	2(11)
C(27)	0.6338(9)	-0.0660(8)	0.2741(6)	34(6)	55(8)	50(7)	18(13)	35(10)	13(13)
C(28)	0.7382(10)	-0.0813(7)	0.2582(7)	38(7)	40(7)	72(8)	23(12)	32(12)	12(13)
C(29)	0.7598(10)	-0.0452(7)	0.1915(7)	38(7)	41(8)	65(7)	17(13)	43(11)	-12(13)
C(30)	0.6756(10)	0.0044(7)	0.1377(6)	48(7)	33(7)	52(7)	0(12)	46(10)	1(12)
C(31)	0.5704(9)	0.0193(7)	0.1533(6)	29(6)	33(7)	44(6)	-6(11)	29(10)	-2(11)
C(32)	0.4680(9)	0.0001(7)	0.1120(6)	43(7)	31(6)	29(6)	11(12)	14(10)	19(11)
N(9)	0.3026(7)	0.2178(5)	0.1988(5)	37(5)	37(5)	27(5)	-15(10)	23(8)	-1(9)
C(33)	0.4083(9)	0.2481(7)	0.2054(6)	31(6)	37(7)	40(6)	-15(12)	14(10)	-14(12)
C(34)	0.4642(11)	0.3067(8)	0.2613(7)	52(8)	46(8)	65(8)	-6(14)	14(14)	3(14)
C(35)	0.4107(11)	0.3387(7)	0.3133(7)	61(8)	32(7)	48(7)	-14(14)	0(13)	-14(13)
C(36)	0.2990(11)	0.3112(7)	0.3062(6)	84(9)	36(7)	41(6)	-13(14)	58(12)	-24(12)
C(37)	0.2474(10)	0.2520(7)	0.2489(6)	44(6)	32(6)	55(7)	-19(13)	49(10)	8(12)
C(38)	0.1629(9)	0.0225(8)	0.0509(6)	50(6)	97(9)	27(5)	-80(14)	66(9)	-33(13)
O(1)	0.1273(8)	-0.0374(5)	0.0109(5)	95(7)	64(6)	67(5)	-35(11)	56(10)	-59(10)

[a] The Debye–Waller factor is defined as $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{33}b^*c^*kl)]$. The values for U have been multiplied by 10^3, except for those of Os, which have been multiplied by 10^4.

respects. In the first place, the source of carbon monoxide is unknown. Since the reaction of $RuCl_3 \cdot 3H_3O$ with phthalonitrile was carried out in air without solvent, there should not be any direct carbonyl sources in the system. In the second place, the major product was four-coordinate $PcRu^{II}$, whereas it appears that stable Ru(II)–porphyrin complexes are generally six-coordinate.[15-20]

This carbonyl complex of ruthenium phthalocyanine can be synthesized in two different ways directly in high yield (80–90%). The reaction of $RuCl_3 \cdot 3H_2O$ with excess phthalonitrile under carbon monoxide atmosphere gives an almost quantitative yield even after the isolation of the compound through column chromatography. The reaction of $Ru_3(CO)_{12}$ with excess phthalonitrile also gives a high yield of $PcRu^{II}(CO)(py)$. These reactions are shown in the following equations:

$$RuCl_3 \cdot 3H_2O + C_6H_4(CN)_2 + CO \rightarrow PcRu^{II}(CO)L \xrightarrow{\text{pyridine}} PcRu^{II}(CO)(py)$$

$$Ru_3(CO)_{12} + C_6H_4(CN)_2 \rightarrow PcRu^{II}(CO)L \xrightarrow{\text{pyridine}} PcRu^{II}(CO)(py)$$

Table VI. Comparison of CO Frequencies (ν(C≡O), cm^{-1}) of MP(CO)(py)[a]

RuPc	RuTPP	OsPc	OsTPP	OsOEP
1965	1939	1930	1920	1902

[a] P = Pc, TPP, and OEP; Pc = phthalocyanine; TPP = tetraphenylporphine; OEP = octaethylporphyrin; py = pyridine; M = Os or Ru.

The carbonyl complex of ruthenium phthalocyanine was characterized by infrared and visible absorption spectroscopy and elemental analysis. The infrared spectrum of the compound shows an intense band at 1965 cm^{-1} which is assigned to ν(C≡O) attached to ruthenium ion.

A well-defined carbonyl complex of osmium phthalocyanine was also isolated from the products of the reported reactions of OsO_4 with molten phthalonitrile.[5] Although the yield of $PcOs^{II}(CO)L$ is less than 5%, it is isolated as a pure complex by column chromatography. The isolation was made possible by the remarkable solubility of the complex in common organic solvents. The presence of a carbonyl ligand attached to osmium metal was evidenced by an intense band at 1930 cm^{-1} in the infrared spectrum. This new type of compound, $PcOs^{II}(CO)L$, coordinates another donor molecule as its last axial ligand. For example, tetrahydrofuran and pyridine can coordinate to the open sixth site of osmium to form a stable compound with octahedral configuration.

These carbonyl complexes of osmium phthalocyanine can be prepared in high yield (80–90%) by the reaction of OsO_4 with molten phthalonitrile in carbon monoxide atmosphere or the reaction of $Os_3(CO)_{12}$ with phthalonitrile in air. Subsequent treatments with pyridine and THF yield $PcOs^{II}(CO)(py)$

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(15) Chow, B. C.; Cohen, I. A. *Bioinorg. Chem.* **1971**, *1*, 57.
(16) Hopf, F. R.; Whitten, G. *J. Am. Chem. Soc.* **1976**, *98*, 7422.
(17) Srivastava, T. S.; Hoffman, L.; Tsutsui, M. *J. Am. Chem. Soc.* **1972**, *94*, 1385.
(18) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. *J. Am. Chem. Soc.* **1973**, *95*, 2141.
(19) Buchler, J. W.; Rohbock, K. *J. Organomet. Chem.* **1974**, *65*, 223.
(20) Buchler, J. W.; Folz, M. *Z. Naturforsch., B* **1977**, *32*, 1439.

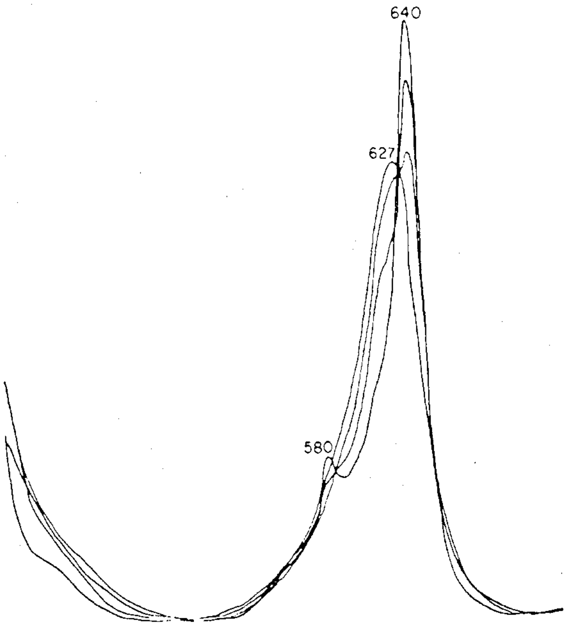
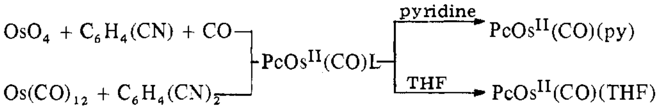


Figure 1. Coordination of carbon monoxide by $PcRu^{II}$ in THF. The peak at 627 nm is characteristic for $PcRu^{II}$ and the peaks at 640 and 580 nm are due to $PcRu^{II}(CO)(THF)$. Upon coordination of carbon monoxide, the peak at 627 nm disappears, while new peaks (at 540 and 580 nm) appear.

and $PcOs^{II}(CO)(THF)$, respectively. Column chromatography gives a single blue band of each complex. An X-ray diffraction analysis has been carried out on the former complex.

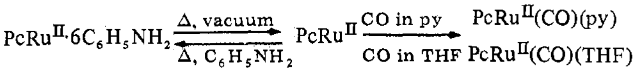


$$\left.\begin{array}{l} OsO_4 + C_6H_4(CN) + CO \\ Os(CO)_{12} + C_6H_4(CN)_2 \end{array}\right\} PcOs^{II}(CO)L \left\{\begin{array}{l}\xrightarrow{\text{pyridine}} PcOs^{II}(CO)(py)\\ \xrightarrow{\text{THF}} PcOs^{II}(CO)(THF)\end{array}\right.$$

Carbonyl complexes of ruthenium and osmium porphines have been synthesized and characterized by a number of workers.[15-20] Table VI summarizes the carbonyl stretching frequencies of these complexes together with those of the carbonyl complexes of ruthenium and osmium phthalocyanines.

Carbonyl(tetraphenylporphinato)(pyridine)ruthenium(II) (TPPRu(CO)(py)) shows a carbonyl peak at 1939 cm^{-1}, which is slightly lower than that (1965 cm^{-1}) of PcRu(CO)(py). Therefore, the back-donation of 4d electrons of ruthenium to the antibonding π orbitals of the carbonyl ligand seems to be less in the phthalocyanine complex than in the TPP complex. The same phenomenon in observed in osmium complexes. Carbonyl(octaethylporphinato)(pyridine)osmium(II) (OEPOs(CO)(py)) shows a carbonyl peak at 1902 cm^{-1}, while PcOs(CO)(py) shows a carbonyl peak at 1930 cm^{-1}. In this case back-donation of 5d electrons from osmium to the antibonding π orbital of the carbonyl ligand seems to be less in the phthalocyanine than in the OEP complex. Probably the structural difference of the rings causes the difference in the degree of the back-donation of d electrons from the central metal ions to the coordinated carbon monoxide. Apparently, Ru(II) or Os(II) in the phthalocyanine carbonyl complexes donates less electron density to the carbonyl ligand than those in porphyrin rings.

It should also be noted that the $PcRu^{II}$ complex, which does not have a carbonyl ligand, is capable of coordinating carbon monoxide at room temperature under 1 atm of carbon monoxide. $PcRu^{II}$ can be prepared by removing aniline molecules from $PcRu^{II}\cdot 6C_6H_5NH_2$ under vacuum at high temperature (200 °C) and it can form a carbonyl complex in THF or pyridine by bubbling CO gas into the solution for 1 day. The original $PcRu^{II}\cdot 6C_6H_5NH_2$ can be recovered by refluxing $PcRu^{II}$ in freshly distilled aniline for a few minutes as shown in the following equation:



$$PcRu^{II}\cdot 6C_6H_5NH_2 \underset{\Delta,\ C_6H_5NH_2}{\overset{\Delta,\ \text{vacuum}}{\rightleftarrows}} PcRu^{II} \begin{array}{l}\xrightarrow{\text{CO in py}} PcRu^{II}(CO)(py)\\ \xrightarrow[\text{CO in THF}]{} PcRu^{II}(CO)(THF)\end{array}$$

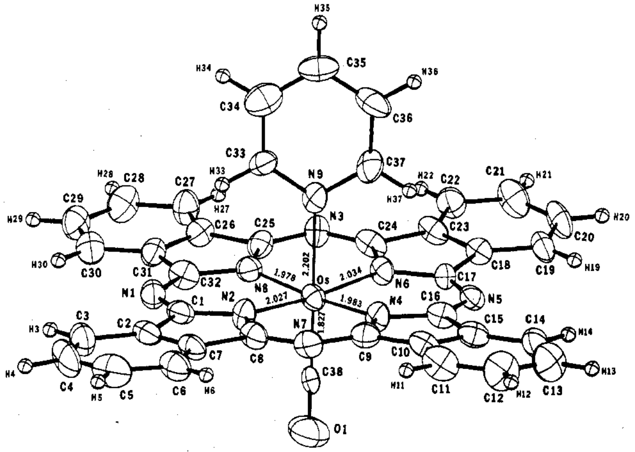


Figure 2. ORTEP[13] drawing of the structure of $PcOs^{II}(CO)(py)$. Numbering scheme is shown. The bond lengths involving the osmium ion are also shown. The thermal ellipsoids are drawn for 50% probability, except those of the hydrogen atoms, which are not drawn to scale.

The carbonylation process can be traced by noting changes in its visible spectrum as shown in Figure 1.

$PcRu^{II}$ is expected to demonstrate an interesting chemistry, because it does not possess a carbonyl ligand. On the other hand, the chemistry of ruthenium porphyrin is rather limited because removal of the carbonyl ligand is extremely difficult.[16,21] $PcRu^{II}$ appears to have the potential to form new ruthenium phthalocyanine complexes with various other molecules such as O_2, N_2, NO, and olefins. Also, the remarkable solubility of ruthenium and osmium phthalocyanine complexes will possibly open a new era in the coordination chemistry of metallophthalocyanines.

Description of Structure of PcOs(CO)(py)

The structure of carbonyl(phthalocyanato)(pyridine)osmium(II) is shown in Figure 2. Stereoviews are shown in Figures 3 and 4. The osmium ion is octahedrally coordinated with the carbonyl and pyridine groups axially coordinated. The pyridine ring is tilted slightly with respect to the perpendicular to the phthalocyanine ring. The interplanar angle is 98.6°.

The structure of an analogous osmium-porphyrin complex has not been reported, but the structure of carbonyl(tetraphenylporphinato)(pyridine)ruthenium(II), TPPRu(CO)(py), has been published.[22] Osmium and ruthenium have similar covalent radii.[23] The phthalocyanine complex bears a strong resemblance to this metalloporphine. In addition, the structure of a carbonyl-osmium-porphodimethene complex with pyridine as the other axial ligand, $OEPMe_2Os(CO)(py)$, has been reported.[24] Interesting comparisons may be made between these two complexes and PcOs(CO)(py).

Bond lengths and angles are given in Table VII. The average interatomic distances between the osmium atom and the isoindole nitrogen atoms of the phthalocyanine molecule are 2.01 Å. However, it should be noted that the bond lengths for Os-N(2) and Os-N(6) are 1.98 Å, while the other two distances are 2.03 Å. The difference corresponds to ~5

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(21) Farrell, N.; Dolphin, D. H.; James, B. R. *J. Am. Chem. Soc.* **1978**, *100*, 324.

(22) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 8583.

(23) Pauling, L. "The Chemical Bond"; Cornell University Press: Ithaca, N.Y., 1967; pp 135-153.

(24) Buchler, J. W.; Lay, K. Lam; Smith, P. D.; Scheidt, W. R.; Rupperecht, G. A.; Kenney, J. E. *J. Organomet. Chem.* **1976**, *110*, 109.

Table VII. Bond Lengths (Å) and Angles (deg)[a]

Os–N(2)	2.027 (9)	2.01 (3)
Os–N(4)	1.983 (9)	
Os–N(6)	2.034 (9)	
Os–N(8)	1.978 (9)	
Os–N(9)	2.202 (9)	
Os–C(38)	1.83 (1)	
N(2)–C(1)	1.38 (1)	1.37 (1)
N(2)–C(8)	1.36 (1)	
N(4)–C(9)	1.39 (1)	
N(4)–C(16)	1.37 (1)	
N(6)–C(17)	1.37 (1)	
N(6)–C(24)	1.36 (1)	
N(8)–C(25)	1.38 (1)	
N(8)–C(32)	1.39 (1)	
N(1)–C(1)	1.33 (1)	1.34 (2)
N(1)–C(32)	1.33 (1)	
N(3)–C(8)	1.35 (1)	
N(3)–C(9)	1.36 (1)	
N(5)–C(16)	1.32 (1)	
N(5)–C(17)	1.32 (1)	
N(7)–C(24)	1.35 (1)	
N(5)–C(25)	1.37 (1)	
C(1)–C(2)	1.46 (1)	1.46 (2)
C(7)–C(8)	1.47 (1)	
C(9)–C(10)	1.45 (2)	
C(15)–C(16)	1.47 (1)	
C(17)–C(18)	1.46 (1)	
C(23)–C(24)	1.47 (2)	
C(25)–C(26)	1.48 (2)	
C(31)–C(32)	1.42 (2)	
C(2)–C(7)	1.40 (2)	1.41 (1)
C(10)–C(15)	1.42 (1)	
C(18)–C(23)	1.41 (2)	
C(26)–C(31)	1.40 (2)	
C(2)–C(3)	1.40 (2)	1.39 (1)
C(6)–C(7)	1.38 (1)	
C(10)–C(11)	1.40 (2)	
C(14)–C(15)	1.38 (2)	
C(18)–C(19)	1.39 (1)	
C(22)–C(23)	1.39 (1)	
C(26)–C(27)	1.37 (2)	
C(30)–C(31)	1.39 (2)	
C(3)–C(4)	1.38 (2)	1.38 (1)
C(5)–C(6)	1.37 (2)	
C(1)–C(12)	1.35 (2)	
C(13)–C(14)	1.38 (2)	
C(19)–C(20)	1.39 (2)	
C(21)–C(22)	1.36 (2)	
C(27)–C(128)	1.38 (2)	
C(29)–C(130)	1.39 (2)	
C(4)–C(5)	1.40 (2)	1.39 (1)
C(12)–C(13)	1.39 (2)	
C(20)–C(21)	1.40 (2)	
C(28)–C(29)	1.39 (2)	
N(9)–C(33)	1.32 (1)	1.34 (3)
N(9)–C(37)	1.36 (2)	
C(33)–C(34)	1.36 (2)	1.36 (1)
C(34)–C(35)	1.36 (2)	
C(35)–C(36)	1.37 (2)	
C(36)–C(37)	1.37 (2)	
C(38)–O(1)	1.17 (1)	
N(2)–N(4)	2.84 (1)	2.83 (1)
N(2)–N(8)	2.82 (1)	
N(4)–N(6)	2.84 (1)	
N(6)–N(8)	2.83 (1)	
N(2)–N(6)	4.06 (1)	4.01 (7)
N(4)–N(8)	3.96 (1)	
N(1)–N(5)	6.78 (1)	6.78 (1)
N(3)–N(7)	6.77 (1)	
N(2)–Os–N(4)	90.1(4)	89.9 (3)
N(2)–Os–N(8)	89.6(4)	
N(4)–Os–N(6)	90.1(4)	
N(6)–Os–N(8)	89.7(4)	
N(2)–Os–N(6)	174.2(4)	174.3 (2)
N(4)–Os–N(8)	174.5(4)	
N(2)–Os–N(9)	88.2(4)	87 (1)
N(4)–Os–N(9)	88.8(4)	
N(6)–Os–N(9)	86.0(4)	
N(8)–Os–N(9)	85.7(4)	
N(2)–Os–C(38)	91.9(5)	93 (1)
N(4)–Os–C(38)	92.3(5)	
N(6)–Os–C(38)	93.8(5)	
N(8)–Os–C(38)	93.2(5)	
N(9)–Os–C(38)	178.9(6)	
Os–N(2)–C(1)	124.3(8)	125 (2)
Os–N(2)–C(8)	124.3(8)	
Os–N(4)–C(9)	125.8(8)	
Os–N(4)–C(16)	126.9(7)	
Os–N(6)–C(17)	123.3(8)	
Os–N(6)–C(24)	123.8(9)	
Os–N(8)–C(25)	126.4(8)	
Os–N(8)–C(32)	127.3(8)	
C(1)–N(2)–C(8)	111(1)	109 (3)
C(9)–N(4)–C(16)	107(1)	
C(17)–N(6)–C(24)	113(1)	
C(25)–N(8)–C(32)	106(1)	
C(1)–N(1)–C(32)	125(1)	125 (1)
C(8)–N(3)–C(9)	126(1)	
C(16)–N(5)–C(17)	124(1)	
C(24)–N(7)–C(25)	125(1)	
N(1)–C(1)–N(2)	128(1)	127 (2)
N(2)–C(8)–N(3)	125(1)	
N(3)–C(9)–N(4)	126(1)	
N(4)–C(16)–N(5)	125(1)	
N(5)–C(17)–N(6)	128(1)	
N(6)–C(24)–N(7)	129(1)	
N(7)–C(25)–N(8)	127(1)	
N(8)–C(32)–N(1)	125(1)	
N(1)–C(1)–C(2)	125(1)	124 (1)
N(3)–C(8)–C(7)	123(1)	
N(3)–C(9)–C(10)	124(1)	
N(5)–C(16)–C(15)	124(1)	
N(5)–C(17)–C(18)	125(1)	
N(7)–C(24)–C(23)	124(1)	
N(7)–C(25)–C(26)	123(1)	
N(1)–C(32)–C(31)	124(1)	
N(2)–C(1)–C(2)	107(1)	109 (2)
N(2)–C(8)–C(7)	108(1)	
N(4)–C(9)–C(10)	110(1)	
N(4)–C(16)–C(15)	111(1)	
N(6)–C(17)–C(18)	106(1)	
N(6)–C(24)–C(23)	106(1)	
N(8)–C(25)–C(26)	110(1)	
N(8)–C(32)–C(31)	111(1)	
C(1)–C(2)–C(7)	108(1)	107 (1)
C(2)–C(7)–C(8)	106(1)	
C(9)–C(10)–C(15)	107(1)	
C(10)–C(15)–C(16)	105(1)	
C(17)–C(18)–C(23)	107(1)	
C(18)–C(23)–C(24)	107(1)	
C(25)–C(26)–C(31)	105(1)	
C(26)–C(31)–C(32)	107(1)	
C(1)–C(2)–C(3)	131(1)	132 (1)
C(6)–C(7)–C(8)	132(1)	
C(9)–C(10)–C(11)	134(1)	
C(14)–C(15)–C(16)	134(1)	
C(17)–C(18)–C(19)	132(1)	
C(22)–C(23)–C(24)	132(1)	
C(25)–C(26)–C(27)	132(1)	
C(30)–C(31)–C(32)	133(1)	
C(7)–C(2)–C(3)	121(1)	121 (1)
C(2)–C(7)–C(6)	121(1)	
C(15)–C(10)–C(11)	119(1)	
C(10)–C(15)–C(14)	121(1)	
C(23)–C(18)–C(19)	121(1)	
C(18)–C(23)–C(22)	120(1)	
C(31)–C(26)–C(27)	122(1)	
C(26)–C(31)–C(30)	120(1)	
C(2)–C(3)–C(4)	116(1)	118 (1)
C(5)–C(6)–C(7)	118(1)	
C(10)–C(11)–C(12)	120(1)	
C(13)–C(14)–C(15)	119(1)	
C(18)–C(19)–C(20)	117(1)	
C(21)–C(22)–C(23)	119(1)	
C(26)–C(27)–C(28)	118(1)	
C(29)–C(30)–C(31)	118(1)	
C(3)–C(4)–C(5)	122(1)	121 (1)
C(4)–C(5)–C(6)	121(1)	
C(11)–C(12)–C(13)	121(1)	
C(12)–C(13)–C(14)	121(1)	
C(19)–C(20)–C(21)	122(1)	
C(20)–C(21)–C(22)	121(1)	
C(27)–C(28)–C(29)	121(1)	
C(28)–C(29)–C(30)	121(1)	
Os–N(9)–C(33)	122.2(9)	121.8 (5)
Os–N(9)–C(37)	121.5(8)	
C(33)–N(9)–C(38)	116(1)	
N(9)–C(33)–C(34)	124(1)	123 (1)
N(9)–C(37)–C(36)	123(1)	
C(33)–C(34)–C(35)	120(1)	119 (1)
C(34)–C(35)–C(36)	118(1)	
C(35)–C(36)–C(37)	119(1)	
Os–C(38)–O(1)	177(1)	

[a] Some nonbonded distances of interest are also given. Figures in parentheses for the averaged values are the root-mean-square standard deviations of the least significant figure.

standard deviations, so it is statistically significant. The C–N–C and N–C–C angles involving the isoindole nitrogen atoms also differ in the two pairs of isoindole groups. Thus, for groups 1 and 3 (containing N(2) and N(6)) the average C–N–C angle is 112°, while the N–C–C angle is 107°. In groups 2 and 4 (containing N(4) and N(8)) the corresponding angles are 107 and 111°. The differences once again correspond to about 4 or 5 standard deviations and are therefore significant. We are unable to offer a plausible explanation for these differences, which are not observed in other phthalocyanine complexes.

The size of the central "hole" in phthalocyanine complexes

Table VIII. Least-Squares Planes

A. Deviations (Å) from Planes

	plane 1	plane 2	plane 3	plane 4	plane 5	plane 6	plane 7
Os	−0.154	−0.099	−0.083	−0.056	0.017	−0.070	
N(1)	−0.082	−0.102	0.044	−0.147	−0.001	0.088	
N(2)	−0.006	0.003	0.025	−0.086	0.248	0.181	
N(3)	0.053	0.074	−0.026	−0.111	0.511	0.297	
N(4)	−0.075	−0.003	−0.090	−0.018	0.251	0.039	
N(5)	−0.157	−0.029	−0.143	0.102	0.102	−0.158	
N(6)	−0.003	0.014	0.180	−0.013	−0.013	−0.117	
N(7)	0.067	0.156	0.288	0.424	−0.053	−0.009	
N(8)	−0.041	−0.004	0.113	0.096	−0.028	0.011	
C(1)	−0.049	−0.068	0.014	−0.176	0.148	0.160	
C(2)	−0.029	−0.075	−0.011	−0.287	0.261	0.258	
C(3)	−0.042	−0.121	−0.016	−0.390	0.240	0.295	
C(4)	0.030	−0.069	0.000	−0.437	0.418	0.437	
C(5)	0.117	0.030	0.028	−0.379	0.615	0.546	
C(6)	0.097	0.043	0.001	−0.309	0.603	0.478	
C(7)	0.020	−0.013	−0.022	−0.267	0.420	0.329	
C(8)	0.014	0.016	−0.018	−0.157	0.389	0.258	
C(9)	0.025	0.078	−0.047	−0.034	0.462	0.209	
C(10)	0.070	0.144	−0.054	0.018	0.600	0.255	
C(11)	0.159	0.228	−0.031	0.021	0.813	0.397	
C(12)	0.111	0.205	−0.115	0.009	0.830	0.333	
C(13)	−0.051	0.075	−0.250	−0.031	0.612	0.102	
C(14)	−0.118	0.013	−0.253	−0.011	0.422	−0.021	
C(15)	−0.062	0.044	−0.159	0.010	0.412	0.052	
C(16)	−0.102	0.001	−0.130	0.035	0.244	−0.031	
C(17)	−0.124	0.002	−0.048	0.196	0.018	−0.166	
C(18)	−0.037	0.118	0.086	0.416	0.014	−0.157	
C(19)	−0.066	0.122	0.049	0.478	−0.009	−0.236	
C(20)	0.039	0.246	0.208	0.699	−0.012	−0.203	
C(21)	0.157	0.353	0.386	0.845	−0.004	−0.106	
C(22)	0.187	0.351	0.423	0.787	0.021	−0.026	
C(23)	0.062	0.205	0.244	0.542	0.001	−0.080	
C(24)	0.021	0.128	0.195	0.387	−0.016	−0.055	
C(25)	0.005	0.060	0.216	0.256	−0.093	−0.012	
C(26)	0.014	0.049	0.279	0.259	−0.178	−0.003	
C(27)	0.083	0.122	0.411	0.412	−0.232	0.011	
C(28)	0.046	0.059	0.411	0.337	−0.333	−0.008	
C(29)	−0.010	−0.027	0.328	0.159	−0.329	0.008	
C(30)	−0.079	−0.102	0.194	0.003	−0.275	−0.007	
C(31)	−0.052	−0.049	0.184	0.069	−0.183	0.003	
C(32)	−0.099	−0.094	0.070	−0.041	−0.106	−0.003	
N(9)							0.020
C(33)							−0.013
C(34)							−0.004
C(35)							0.013
C(36)							−0.005
C(37)							−0.011

B. Angles (deg) between Least-Squares Planes

plane	plane 2	plane 3	plane 4	plane 5	plane 6	plane 7
1	1.4	2.7	5.2	5.1	3.1	98.6
2		3.0	4.1	5.5	4.2	98.0
3			4.1	7.9	5.3	96.1
4				9.4	8.3	94.1
5					3.7	103.4
6						101.4

C. Equations of Planes[a]

Plane 1 Marcocycle; N(1), N(8), C(1)–C(32)
$2.721x + 12.314y + 8.382z = 3.126$

Plane 2 Isoindole Nitrogen Atoms; N(2), N(4), N(6), N(8)
$2.509x + 12.216y + 8.726z = 3.053$

Plane 3 Isoindole Group 1; N(2), C(1)–C(8)
$3.051x + 11.869y + 8.660z = 3.113$

Plane 4 Isoindole Group 2; N(4), C(9)–C(16)
$2.438x + 11.516y + 9.693z = 3.029$

Plane 5 Isoindole Group 3; N(6), C(17)–C(24)
$2.125x + 13.099y + 7.731z = 2.833$

Plane 6 Isoindole Group 4; N(8), C(25)–C(32)
$2.836x + 12.756y + 7.589z = 3.024$

Plane 7 Pyridine Ring; N(9), C(33)–C(37)
$2.361x - 11.469y + 9.817z = 0.148$

[a] All planes are unweighted. *x, y, z* are in monoclinic fractional coordinates.

has been estimated to be 0.046–0.050 Å smaller than in corresponding porphyrin complexes.[25] A similar difference is noted in the present case. The osmium atom is slightly out of the plane of the phthalocyanine molecule, so the size of the hole has to be estimated from the distances between opposite isoindole nitrogen atoms. These distances are 4.06 and 3.96

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(25) Kirner, J. F.; Dow, W.; Scheidt, W. R. *Inorg. Chem.* **1976**, *15*, 1685.

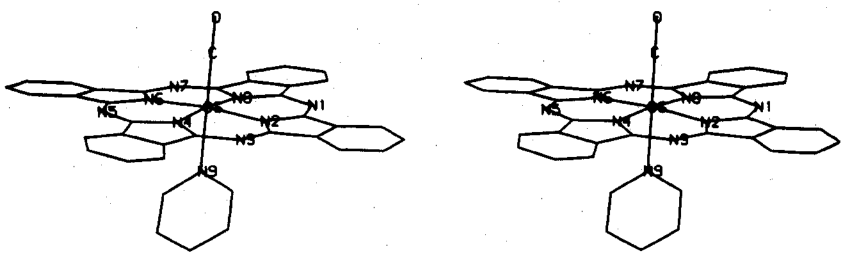

Figure 3. Stereoview of $PcOs^{II}(CO)(py)$.

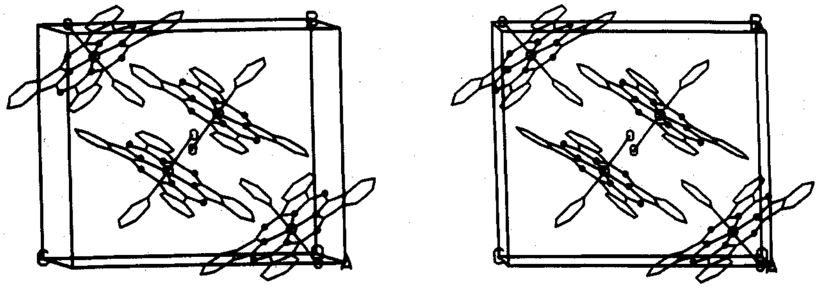

Figure 4. Stereoview of the packing in the unit cell. The osmium atoms are indicated by the smaller circles. Oxygen atoms of the carbonyl groups are labeled with the letter O.

Å, corresponding to an average radius (Ct–N distance) of 2.01 Å for the macrocyclic hole. In TPPRu(CO)(py)[22] the corresponding distance is 2.05 Å. The M–N distances are correspondingly longer. In both TPPRu(CO)(py)[22] and $OEPMe_2Os(CO)(py)$[24] these average 2.06 Å.

The Os–N bond lengths involving the isoindole nitrogen atoms are short for such bonds. On the other hand the $Os-N_{py}$ (N_{py} is the pyridine nitrogen atom) distance of 2.209 (9) Å is relatively long. $Ru-N_{py}$ distances of 2.06–2.09 Å have been reported.[26] $M-NH_3$ bond lengths in amine complexes of Os(II) and Ru(II) range from 2.12 to 2.14 Å.[26–29] The $M-N_{py}$ distance in both TPPRu(CO)(py) and $OEPMe_2Os(CO)(py)$ is also elongated (2.193 (4) and 2.230 (4) Å, respectively).

This long bond may be due to steric interactons between atoms in the pyridine ring, particularly the α-hydrogen atoms, and atoms in the macrocycle. This would block a closer approach to the osmium atom by the pyridine molecule. The osmium atom lies 0.15 Å on the other side of phthalocyanine molecule. However, the closest contacts involving the α-hydrogen atoms are between H(33) and C(32) and between H(37) and C(16). These contacts are both about 2.73 Å, which is not an unusually short contact distance in such cases. A tabulation of such contacts in porphyrin complexes containing planar axial ligands shows a range of 2.45–2.9 Å.[30] In TPPRu(CO)(py) the closest contact is 2.51 Å.

The angle between the plane of the pyridine ring and the plane defined by N(2), Os, and N(6) is 48°. An angle of $\sim$45° minimizes steric interaction, whereas an angle of $\sim$0° would bring the α-hydrogen atoms into close contact with the isoindole nitrogen atoms.[31]

It has also been suggested a lengthening of $\sim$0.1 Å will occur in the axial M–N bond due to the trans effect of the carbonyl group.[22] In $OEPRu(py)_2$[32] the observed axial bond lengths are indeed shorter, 2.09–2.10 Å, in spite of some relatively close contacts of the α-hydrogen atoms of the pyridine ligands with atoms in the macrocycle.[30] An even shorter M–N bond length of 2.00 Å has been reported in $PcFe(py)_2$.[33]

The metal carbonyl distance of 1.83 (1) Å is in good agreement with the values found in TPPRu(CO)(py) and $OEPMe_2Os(CO)(py)$. The Os–C–O angle is linear (177°).

Least-squares planes of interest are given in Table VIII. As mentioned previously, the osmium atom is 0.15 Å out of the plane defined by the phthalocyanine group in a direction toward the carbonyl group. The displacement decreases to 0.099 Å if one considers only the plane of the four isoindole nitrogen atoms. By way of comparison, the ruthenium atom in TPPRu(CO)(py) is 0.079 Å out of the plane of the porphyrin skeleton toward the carbonyl group.

In the discussion of TPPRu(CO)(py) the authors attributed the out-of-plane displacement of the metal ion either to very strong metal–carbonyl bonds or to the inability of the large metal ion to fit into the plane of the macrocycle.[22] The former possibility now appears more likely, since in $OEPRu(py)_2$ the ruthenium(II) ion lies in the plane of the macrocycle. The same factor is probably primarily responsible for the out-of-plane displacement observed for the metal ion in this phthalocyanine complex.

The difference of 0.065 Å in the displacements of the metal ion from the planes of the macrocycle and of the isoindole nitrogen atoms indicates that the macrocycle itself is "domed", corresponding to a C_{4v} deviation from planarity. Deviations of equal or larger magnitude have been observed in other metallophthalocyanine complexes, where the metal ion is out of the plane of the macrocycle.[34–37] The difference between the deviation of the osmium atom from the plane of the four isoindole nitrogen atoms and the plane defined by the pyrrole rings and the bridging nitrogen atoms is 0.027 Å, a value falling in the middle of the range found for porphyrins with

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(26) Cheng, P. T.; Loescher, B. R.; Nyburg, S. C. *Inorg. Chem.* **1971**, *10*, 1275.

(27) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.

(28) Fergusson, J. E.; Love, J. L.; Robinson, W. T. *Inorg. Chem.* **1972**, *11*, 1662.

(29) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1078.

(30) Cullen, D. L.; Meyer, E. F., Jr. *Acta Crystallogr., Sect. B* **1973**, *29*, 2507.

(31) Collins, D. M.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2066.

(32) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.*, **1975**, *97*, 277.

(33) Kobayashi, T.; Kurokawa, F.; Ashida, T.; Uyeda, N.; Suito, E. *J. Chem. Soc.* **1971**, 1963.

(34) Freidel, M. K.; Hoskins, B. F.; Martin, R. L.; Mason, S. A. *J. Chem. Soc.* **1970**, 400.

(35) Kobayashi, T.; Ashida, T.; Uyeda, N.; Suito, E.; Kakudo, M. *Bull Chem. Soc. Jpn.* **1971**, *44*, 2095.

(36) Fischer, M. S.; Templeton, D. H.; Zalkin, A.; Calvin, M. *J. Am. Chem. Soc.* **1971**, *93*, 2622.

(37) Ukei, K. *Acta Crystallogr., Sect. B* **1973**, *29*, 2290.

Table IX. Intermolecular Contacts (Å) ≤ 3.5 Å[a]

C(16)–O(1)$^{\mathrm{I}}$	3.08	N(3)–C(35)$^{\mathrm{II}}$	3.32
O(1)–O(1)$^{\mathrm{I}}$	3.18	N(5)–C(4)$^{\mathrm{III}}$	3.40
N(4)–O(1)$^{\mathrm{I}}$	3.25	C(23)–C(35)$^{\mathrm{IV}}$	3.41
C(15)–O(1)$^{\mathrm{I}}$	3.26	C(24)–C(36)$^{\mathrm{IV}}$	3.42
C(38)–O(1)$^{\mathrm{I}}$	3.31		

[a] Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z: (I) $-x, -y, -z$; (II) $-^1/_2 + x, ^1/_2 - y, -^1/_2 + z$; (III) $-^1/_2 + x, ^1/_2 - y, ^1/_2 - z$; (IV) $1 - x, -y, -z$.

the metal ion out of the macrocyclic plane.[38]

The doming is not equal for the four isoindole groups. The maximum deviations from the plane of the four isoindole nitrogen atoms are 0.23 and 0.35 Å for phenyl carbon atoms in groups 2 and 3, while the maximum deviations in the same direction in groups 1 and 4 are 0.04 and 0.12 Å. Such a pattern was observed in aquo(phthalocyanato)magnesium(II).[36]

There appears to be some variation in bond parameters of phthalocyanine complexes as the size of the central "hole" increases.[39] The C–N–C angle involving the azamethine nitrogen atom is the most sensitive bond parameter. This angle ranges from 121.7° in Fe(Pc)[25] (Ct–N = 1.93 Å) to 126.2° in $Cl_2Sn(Pc)$[40] (Ct–N = 2.05 Å). The average value of 125 (1)° found for this angle in PcOs(CO)(py) agrees with that found in phthalocyanine complexes with similar Ct–N distances.[35,39] The presence of a very heavy metal atom like osmium decreases the accuracy with which the lighter atoms can be determined, but within the observed standard deviations, the other bond parameters agree with those reported in the accurately determined structure of Zn(Pc)[39] and Sn(Pc).[34]

A packing diagram of the unit cell is shown in Figure 3. Table IX lists the intermolecular contacts ≤3.5 Å. Most of the shortest contacts involve the carbonyl oxygen atom. Nonbonded contacts of this magnitude have been observed in other carbonyl complexes (e.g., $[H_3OEP]^+[Re_2(CO)_6Cl_3]^-$).[41] Neither these nor any of the other intermolecular contacts are believed to have any significant effect on the structure.

The structure of PcRu(CO)(py) probably possesses a structure similar to that of PcOs(CO)(py).

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Registry No. PcRu(CO)(THF), 71870-08-1; PcRu(CO)(py), 67588-47-0; PcOs(CO)(THF), 71870-09-2; PcOs(CO)(py), 71870-10-5; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; OsO_4, 20816-12-0.

Supplementary Material Available: Tables III–V containing calculated hydrogen atom positions, root-mean-square components of thermal ellipsoids, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(38) Cullen, D. L.; Meyer, E. F., Jr.; Smith, K. M. *Inorg. Chem.* **1977**, *16*, 1179.

(39) Scheidt, W. R.; Dow, W. *J. Am. Chem. Soc.* **1977**, *99*, 1101.

(40) Rogers, D.; Osborn, R. S. *J. Chem. Soc.* **1971**, 840.

(41) Hrung, C. P.; Tsutsui, M.; Cullen, D. L.; Meyer, E. F., Jr.; Morimoto, C. N. *J. Am. Chem. Soc.* **1978**, *100*, 6068.

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Crystal and Molecular Structures of Two Square-Pyramidal Rhodium(I)–Sulfur Dioxide Complexes. Bonding Effects in Pyramidal-SO_2 Complexes

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The molecular structures of $Rh(ttp)Cl(SO_2)$ and $[Rh(ttp)(CO)(SO_2)](AsF_6)$, where ttp is bis(3-(diphenylphosphino)propyl)phenylphosphine, have been deduced by single-crystal X-ray diffraction. Both compounds contain square-pyramidal coordination units with apical pyramidal sulfur dioxide ligands. The neutral chloride compound is the most dissociatively and oxidatively stable pyramidal sulfur dioxide–metal complex yet reported and also has the shortest known metal–pyramidal SO_2 distance, 2.326 (5) Å. An M–SO_2 distance of 2.433 (6) Å is found for the carbonyl complex, which contains labile, reactive sulfur dioxide. A difference of about 90° is found in the orientation of the SO_2 group relative to the RhP_3L unit, an effect which is related to the π-bonding characteristics of L. A trans influence of 0.10 Å is seen for the Rh–P distance trans to Cl or CO, and the metal is only 0.08 Å out the basal plane for the carbonyl but 0.26 Å out of the plane for the chloride. These structural and chemical features are related to the donor/acceptor nature of Cl and CO. Crystal data: $Rh(ttp)Cl(SO_2)$, $P2_1/a$, $Z = 4$, $a = 21.327$ (8) Å, $b = 11.244$ (3) Å, $c = 14.617$ (6) Å, $\beta = 105.05$ (2)°, $R = 0.056$ for 3515 reflections with $I \geq 2\sigma(I)$; $[Rh(ttp)(CO)(SO_2)](AsF_6)$, $P2_1/c$, $Z = 4$, $a = 11.138$ (8) Å, $b = 19.995$ (2) Å, $c = 20.229$ (2) Å, $\beta = 115.61$ (6)°, $R = 0.084$ for 2295 reflections with $I \geq 2\sigma(I)$.

Introduction

The nature of the chemical bonding of sulfur dioxide to transition metals and other substrates continues to be a prime research area. In particular, there is much interest in determining those factors which dictate the mode of transition metal–SO_2 bonding (pyramidal, coplanar, or side-on-bonded SO_2) and the reactivity of the attached SO_2 (e.g., oxygen sensitivity or lability).[1-8] A recent study by Meek, Blum, and co-workers attempted to address the latter subject by examining a series of Rh(I) complexes of the type $[Rh(ttp)L(SO_2)]^{n+}$, where ttp is the triphosphine bis(3-(diphenyl-

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(1) Eller, P. G.; Kubas, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 4346.

(2) Eller, P. G.; Kubas, G. J. *Inorg. Chem.* **1978**, *17*, 894.

(3) Ryan, R. R.; Eller, P. G. *Inorg. Chem.* **1976**, *15*, 494.

(4) Moody, D. C.; Ryan, R. R. *Inorg. Chem.* **1977**, *16*, 2473.

(5) Eller, P. G.; Ryan, R. R.; Moody, D. C. *Inorg. Chem.* **1976**, *15*, 2442.

(6) Mingos, D. M. P. *Transition Met. Chem.* **1978**, *3*, 1.

(7) Valentine, J.; Valentine, D., Jr.; Collman, J. P. *Inorg. Chem.* **1971**, *10*, 219

(8) Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182.