method has been reviewed recently by Sonesson[16] and has been used so frequently in recent years that no further discussion should be necessary. The constants are listed in Table II.

Discussion

In Fig. 1, log k_1 for the rare earth glyoxylates has been compared to log k_1 for the acetates[17] and the glycolates.[4,5] It is readily apparent that the affinity of the glyoxylate anion for a given rare earth cation is greater than the affinity of the acetate anion, but is less than the affinity of the glycolate anion. One must conclude, therefore, that either the hydrated glyoxylate ion is not really a *gem*-diol, or that the effect of adding a second hydroxyl ion to the α-carbon is to weaken the affinity of the carboxyl group for the rare earth. The latter alternative appears to be the most logical in view of the fact, previously mentioned, that the glyoxylate anion has less affinity for the hydrogen ion than the glycolate anion does.

The stability trend in the rare earth glyoxylate series is more like the trend observed in the glycolate series than that observed in the acetate series. The ratio of k_1 to k_2, however, indicates that the glyoxylate ligand is probably less bidentate in character than the glycolate or lactate ligands. It does not appear that glyoxylate buffer solutions would be of any great value in the ion-exchange separation of rare earths.

The position of yttrium in the rare earth glyoxylate stability sequence is about the same as in the glycolate and lactate sequences, *i.e.*, yttrium tends to resemble terbium and dysprosium.

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Properties and Infrared Spectra in the Potassium Bromide Region of 8-Quinolinol and Its Metal Chelates

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The infrared absorption spectra in the 11–25 μ region of 8-quinolinol and the 8-quinolinol chelates of the alkaline earth ions, manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II), aluminum(III), iron(III), thorium(IV), and uranium(VI) have been recorded and band assignments have been made. A consideration of the spectral shifts has been used to study the structures of the divalent metal chelates in the solid phase. The spectral data indicate that the divalent ions which have available d-orbitals bond differently with 8-quinolinol from those without available d-orbitals. The "solvate" oxine in the thorium(IV) and uranium(VI) chelates is not distinguishable from the "ligand" oxines on the basis of the infrared data. Structures for the α and β forms of copper oxinate are proposed.

Although the infrared absorption spectra of 8-quinolinol (8-hydroxyquinoline; oxine) and its chelates have not been examined in the potassium bromide region (11 to 25 μ), several groups have considered the spectra of these compounds in other regions; both as saturated solutions in carbon tetrachloride[1] and as crystals.[2-5] In addition there has been much interest in the structures of the various metal oxinates. X-Ray studies have been made of the dihydrates of zinc oxinate[6,7] and copper oxinate[8] as well as of anhydrous copper oxinate.[9] Bis(8-quinolinol-5-sulfonic acid)zinc(II) has been shown to be tetrahederal by resolving its optical isomers.[10] The reaction of copper(II) ion with oxine under various solution conditions results in two forms of anhydrous copper oxinate[11] which have distinctive color, density, infrared spectra, and magnetic moments. Several groups have discussed the nature of the bonding of the "extra" oxine molecule in thorium pentaoxinate ($Th(Ox)_4\cdot HOx$) and uranium trioxinate ($UO_2(Ox)_2\cdot HOx$).[12-14]

The present discussion is concerned with the infrared absorption spectra of these compounds in the potassium bromide region and the interpretation of the spectra in terms of bonding and structures. The oxinates of the alkaline earths, the divalent transition metals, lead(II), aluminum(III), iron(III), thorium(IV), and uranium(VI) have been studied as well as the two forms of copper oxinate.

Experimental

Equipment.—The infrared spectra were recorded with a Perkin-Elmer Model 421 recording spectrophotometer equipped with a potassium bromide, linear wave length interchange. The

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TABLE I

ABSORPTION FREQUENCIES OF OXINE AND ITS CHELATES IN THE POTASSIUM BROMIDE REGION[a]

Absorption frequency, cm.$^{-1}$																	
								Cu									
Oxine	Mg	Ca	Sr	Ba	Mn	Co	Ni	α	β	Zn	Cd	Pb	Al	Fe(III)	Th(IV)	U(VI)	Band assignment
812	819	818	818	817	819	819	817	817	850 w	819	817	815	820	819 s	819	818	o.p. C–H bend
805 sh	798	796	796	793	798	798	798	798	825	798	798	796	801	798	798	798	
775	783	782	782	780	781	780	780	780	815 s 798 793 w 775 s	780	781	780	782	780 s	783	780	
...	734	738	745	743	...	...	...	...	...	...	...	...	...	...	...	...	M–OH_2 str.[b]
737	743	740	735	737	743	743 739	743	742	737	744	739	748 sh 740	746 b	746	743	748	i.p. ring def.
706	729	719	716	714	724	729	731	720	729	729	724	723	746 b	734 s	727	729	i.p. ring def.
635	648 641	649	651	654	645	643	646	641	641	645	646	643	644	639	644 w	641 w	i.p. ring def.
573	582	589 w 594	587 w 592 w	585 588	596	599	618 w 604 w 594 w	629	629	602	599 w	587 w	575 w	617 s	604 585 w	599 582 w	i.p. ring def.
544	...	558	553	550	575	580 w	568 w	582 w	578 w	562 w	561 w	554 w	546 s	522 s	505 s	506 s	O–D sens. ring
491	500	489	481	478	505	508	497 w	528 w	528 w	503 w	491 b	494	...	515 w	...	...	O–D sens. ring
470	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	i.p. ring def.
465	506	501	495	493	492 s	503 s	502 s	520 s	520 s	497 s	491 s	483	524	496 w	485	486	i.p. C–O bend
421	...	...	...	...	...	...	...	...	...	...	...	...	458 421	...	...	...	ring def.

[a] The following symbols are used in the table: o.p., out-of-plane; i.p., in-plane; str., stretch; def., deformation; sens., sensitive; s, strong; m, medium; w, weak; b, broad; sh, shoulder. [b] Unheated compounds only.

instrument was calibrated with appropriate air peaks as suggested by the manufacturer. The recorded spectra are believed to be accurate to within ±2 cm.$^{-1}$.

The solid complexes were run as pressed disks using KBr as the diluent.[15] Approximately 3 mg. of sample was mixed for 20 sec. with 0.5 g. of dry KBr using a dentist's amalgamator. The resulting mixture was placed in a 0.5-in. die assembly and evacuated prior to applying a pressure of 25,000 p.s.i. This was applied for 2 min. at room temperature, then the pressure was released and the die assembly rotated 90° while still under vacuum. The die was again brought under pressure for an additional 2 min.

Reagents.—The reagents used in the preparation of the chelates were reagent grade in all cases and were used without further purification.

Preparation of the Metal Oxinates.—The alkaline earth oxinates were prepared by the method of Charles,[16] using the nitrate salts to introduce the alkaline earth ions. One set of the crystals, precipitated from the basic oxine solution and washed with hot water, was dried at room temperature for 1 week, while another set of the crystals was dried at 210° *in vacuo* overnight before its infrared spectrum was recorded.

The divalent metal oxinates were prepared according to standard methods[17] by adding increments of dilute ammonium hydroxide to the metal nitrate salt in glacial acetic acid. The crystals were filtered and washed with methanol to remove any excess oxine. These compounds were dried at 110° for 3 hr. One portion of these crystals later was dried at 210° *in vacuo* overnight before its spectrum was recorded.

α and β copper-oxinate were prepared by the method of Fanning and Jonassen,[11] using the acetate salt and oxine in absolute methanol. The green precipitate which formed immediately was filtered and washed with methanol to remove any excess oxine. The β form was obtained in the same manner, except the green precipitate was allowed to remain in solution for 4 days at room temperature. The black, well-defined crystals which formed were then filtered, washed in methanol, and dried. Both sets of crystals were dried at 110° for 4 hr. The color and infrared spectra of these compounds were identical with those published by Fanning and Jonassen.[11]

The oxinates of aluminum(III), iron(III), and thorium(IV) were prepared in the same manner as the divalent metal oxinates.[17] The nitrate salts of aluminum(III) and iron(III) and the perchlorate salt of thorium(IV) were the source of metal ions. In the case of thorium, orange crystals of thorium pentaoxinate ($Th(Ox)_4 \cdot HOx$) were produced. These orange crystals were recrystallized in methanol and dried at 110° for 4 hr. The yellow thorium tetraoxinate ($Th(Ox)_4$) crystals were prepared by heating the orange crystals at 210° *in vacuo* overnight.

The uranyl oxinates were prepared by homogeneous precipitation[18] using the nitrate salt. The dark red crystals which formed were filtered, washed with methanol and water, and dried at 100° overnight. The green uranyl dioxinate ($UO_2(Ox)_2$) crystals were prepared by heating the red uranyl trioxinate ($UO_2(Ox)_2 \cdot HOx$) crystals at 210° *in vacuo* overnight.

Results

The absorption spectrum of oxine in the KBr region is shown in Fig. 1, curve A. The absorption frequencies of the twelve major peaks are tabulated in Table I.

The alkaline earth oxinates exhibit approximately the same absorption bands as oxine, but they are shifted slightly due to chelation. An absorption spectrum for calcium oxinate, which is representative of this group of chelates, is shown in Fig. 1, curve B. The alkaline earth oxinates have two peaks in the 580 to 590 cm.$^{-1}$ region which appear to correspond to the 573 cm.$^{-1}$ peak of oxine. This splitting is less pronounced for the magnesium chelate and is not observed for the other metal oxinates. The hydrated alkaline earth oxinates have a unique series of peaks in the 730 to 745 cm.$^{-1}$ region of the spectrum. The absorption frequencies of these compounds are tabulated in Table I.

The absorption spectra of the divalent metal oxinates are similar to those of the alkaline earth chelates. Nickel oxinate (Fig. 1, curve C) has some weak bands in the 600 cm.$^{-1}$ region which are not easily observed for the other chelates, but this probably is due to the weak and broad nature of the peaks. Cobalt(II) and thorium(IV) oxinate which have not been washed to

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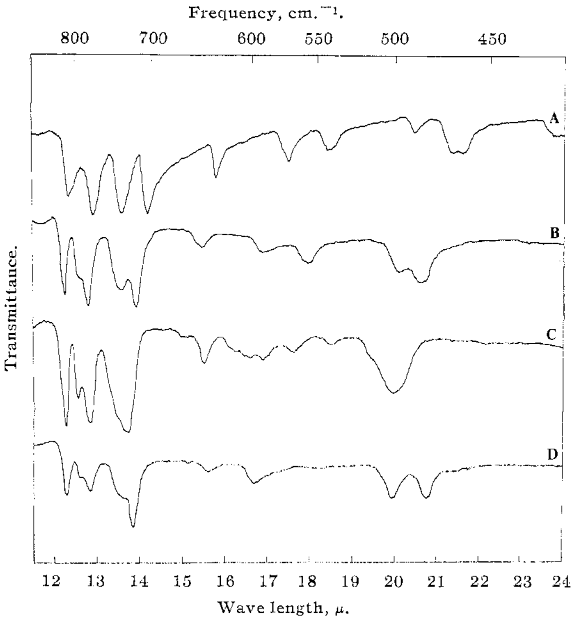

Fig. 1.—Spectra of oxine (curve A), calcium oxinate (curve B), nickel(II) oxinate (curve C), and thorium(IV) oxinate ($Th(Ox)_4 \cdot HOx$) (curve D) in the KBr region of the spectrum.

remove the extra oxine show peaks for oxine as well as the peaks for the chelate. Thus the KBr region can be used to determine free ligand impurities in the oxine chelates.

The α form of copper oxinate has the same absorption bands as the other divalent metal oxinates, but the β form has some unique peaks above 650 cm.$^{-1}$. Below 650 cm.$^{-1}$, however, the spectra of both forms appear identical.

Some of the divalent metal chelates appear to have two peaks superimposed in the 450 to 525 cm.$^{-1}$ region of the spectrum. While this is most pronounced for cadmium oxinate, it is also observed to a lesser extent for nickel, zinc, and cobalt oxinates. The absorption frequencies of the divalent metal oxinates also are tabulated in Table I.

In general, the absorption spectra of the higher valent metal oxinates are the same as those of the other oxinates except greater spectral shifts are observed (see Table I). The spectrum of aluminum oxinate is unique in that it shows two peaks in the 400 cm.$^{-1}$ region which appear to correspond to the peaks of oxine. However, if free oxine were present, other peaks due to oxine would be observed. $Th(Ox)_4 \cdot HOx$ does not show any unique bands in its spectrum, which is identical with the spectrum of $Th(Ox)_4$ (Fig. 1, curve D). The same can be said for $UO_2(Ox)_2 \cdot HOx$ and $UO_2(Ox)_2$.

Discussion and Conclusions

Because the KBr region (about 900 to 400 cm.$^{-1}$) overlaps the NaCl region (about 4000 to 650 cm.$^{-1}$), the results of this study can be compared with the results of other workers in the 900 to 650 cm.$^{-1}$ region. In general, the spectra recorded agree with those of Stone,[2] Charles and co-workers,[3] and Fanning and Jonassen.[11] However, Charles' group reports some absorption peaks not observed in the present study. By assuming that his group worked with hydrated chelates some of the anomalies can be explained. The other unique peaks observed by Charles and co-workers may be due to differences in crystal structure since their spectra were run as mulls.

Absorption Band Assignments.—Because no previous assignments have been made for the absorption bands of oxine in the KBr region, correlations for the various peaks are of interest. A rigorous normal coordinate treatment of the oxine molecule is beyond the scope of this study. However, the correlations shown in Table I can be made using a less rigorous semi-empirical approach based on that used by Karr, Estep, and Papa[19] for out-of-plane bending modes of various compounds. The model compounds which have been used are various substituted pyridines,[20,21] naphthalenes,[22] benzenes,[23] and phenols,[24] whose vibrations have been assigned by normal coordinate type calculations in the literature.

Spectral Shifts.—Charles and co-workers[3] have found for a series of divalent metal oxinates that a plot of absorption frequency as a function of the atomic weight of the metal atom for a peak ascribed to a carbon–oxygen vibration yields two lines with different slopes. One line joins the positions of the oxinates of magnesium, calcium, zinc, cadmium, and lead; the other the oxinates of manganese, copper, nickel, and probably cobalt. To explain this they postulated that oxinates with metal atoms which have no available d-orbitals have a different crystal structure from those with available d-orbitals.

A similar plot has been made in the present study using the absorption band near 460 cm.$^{-1}$ for oxine, which is assigned to an in-plane carbon–oxygen bend. On chelation, this band is shifted to the 480 to 500 cm.$^{-1}$ region. Because this band shows a greater shift than the band plotted by Charles,[3] it is possible not only to substantiate the shift, but also to assign cobalt to a group. The use of ionic radii in place of atomic weights yields the same type of plot. A similar plot also is obtained for the O–D sensitive ring distortion bands[24] at 491 and 544 cm.$^{-1}$ for oxine. The ring distortion band at 573 cm.$^{-1}$ for oxine also shifts in this same general manner, but the data do not give as linear a plot as for the other peaks.

Group one consists of copper, nickel, cobalt, and manganese oxinates. X-Ray studies[9] have shown that anhydrous copper oxinate is square-planar. Because these metal ions all have d-orbitals available for dsp^2 bonding (although magnetic evidence shows they may not be used[23]), it is reasonable to postulate that they form square-planar complexes with oxine. On the other hand, on the basis of the work of Liu and Bailar,[10]

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anhydrous zinc oxinate is believed to be tetrahedral. Because all of the divalent metal ions of group two (zinc, cadmium, lead, and the alkaline earths) do not have available d-orbitals, their bonding with oxine can reasonably be postulated to be tetrahedral (sp^3).

The Effect of Hydration on the Infrared Spectra.—The divalent metal oxinates[25] dried at 110° and the alkaline earth oxinates dried at room temperature should be hydrated when their spectra are determined.[16] Fujita and co-workers[26] have considered the absorption bands due to coordinated water which appear in the NaCl region. They suggest that if the water molecule is ionically bonded to the chelate, the broad bands of water vapor are observed, but if the water molecule is covalently bonded to the metal ion, and also hydrogen bonded to the ligand, sharper absorption peaks are observed.

The oxinates of the alkaline earths show unique absorption bands in the 730 to 745 cm.$^{-1}$ region when they are hydrated. The other hydrated chelates do not show any new or shifted bands. This unique absorption band of the alkaline earth oxinates corresponds to one which Fujita and co-workers[26] assigned to a metal–water stretching mode of nickel glycinate dihydrate. Merritt[7] has shown that the hydrated divalent metal oxinates have water above and below the plane which contains the ligands. With this configuration, it would be difficult for the waters to hydrogen-bond with the ligand. However, if the hydrated alkaline earth oxinates do not adopt this configuration (due to their weaker nitrogen interaction), the water molecules may interact more easily with the ligand and thus cause a sharp absorption band to be observed. Table I lists the absorption peaks which have been assigned to a metal–oxygen stretching mode for these hydrated chelates.

The Two Forms of Copper Oxinate.—In 1957, Suito and Sekido[27] prepared two forms of copper oxinate. Fanning and Jonassen[11] have investigated these two forms further, finding that they differ in color, magnetic moment (α 1.95 B.M. and β 1.73 B.M.), and their infrared absorption. They speculate on the differences between the two forms, but make no real conclusions.

Below 650 cm.$^{-1}$ the spectra of both forms of copper oxinate appear identical. In the 750 to 850 cm.$^{-1}$ region, however, the β form shows three unique absorption bands which appear to be due to C–H bending modes, and in the 700 to 750 cm.$^{-1}$ region the β form shows smaller spectral shifts than the α form.

Kanamaru and co-workers[9] have shown that copper oxinate has a square-planar crystal structure, but they did not specify which form they used. From a consideration of their method of preparation, it appears they used the β form. Fanning and Jonassen[11] suggest that one of the possible differences of the two forms may be that the β form is square-planar, while the other is tetrahedral. This appears to be consistent with the magnetic data, but can be questioned on the basis of the infrared data. Assuming that the spectral plots discussed in the previous section can be used to distinguish crystal structures of the metal oxinates, the position of the α form of copper oxinate on such a plot is essentially the same as the position of the β form. Because the spectra of the two forms are identical below 650 cm.$^{-1}$, both forms appear to have essentially the same crystal structure, although one form may be slightly distorted.

An explanation for the difference between the two forms is that the α form may chelate oxine in a *cis*-planar configuration, which is common for the hydrated divalent oxinates examined by Merritt.[7] Fanning and Jonassen[11] have shown that the α form will only precipitate from acid solutions containing basic anions, and the β form is the sole precipitate from basic solutions. The α form can be converted into the β form by heating to 210°. Thus it appears that α copper oxinate is formed by a reaction mechanism which differs from that of the β form and may thus lead to a *cis*-planar structure, which can be converted to the *trans*-planar structure on heating. Because copper ion forms the strongest oxinate of the divalent metals, on the basis of stability constants[28] and spectral shifts, this type of behavior could reasonably be assumed to take place.

The "Extra" Oxine of Thorium and Uranium Oxinate.—It is well known that certain higher valent metal ions form oxinates of the form $M(Ox)_n \cdot HOx$, where the metal ion, M^{n+}, is scandium(III), thorium(IV), uranium(VI), uranium(IV), or plutonium(VI).[29] Although many of these systems have been studied by a variety of different methods, the nature of the "solvent molecule"–metal chelate interaction is still not well understood. Some workers feel that the interaction is the same for the uranium(VI) and thorium(IV) systems,[12,30] while others feel the interaction is different.[14,31] Moeller and Ramaniah[12] feel that the "extra" oxine molecule is held by weak lattice forces. This opinion is also held by Van Tassel and Wendlandt.[13] Bullwinkel and Nobel[14] have considered the uranium(VI) system and feel that the third oxine is an integral part of the chelate and not distinguishable from the other two. A planar structure is suggested for the chelate with only the uranyl oxygens above and below the plane.

In the NaCl region of the spectrum it is difficult to detect free oxine in the presence of the metal oxinates, but experiments with chelates containing excess oxine have shown that this is easily done in the KBr region. Thus if the "extra" oxine of thorium and uranium oxinate were held to the chelate by crystal lattice forces, the vibrational bands of free oxine should be observed in the KBr region for these compounds. If, however, the oxine molecule is an integral part of the complex,

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the spectra of the "solvated" chelates should not show any oxine bands and probably would resemble the spectra of the "unsolvated" chelate. The latter is the case for both the thorium(IV) and the uranium(VI) systems as shown in Fig. 1, curve D, and Table I. Thus a structure such as that proposed by Bullwinkel and Nobel[14] appears to be quite reasonable for the uranyl system. For the thorium(IV) system, this may indicate a coordination number of ten.

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The Infrared Spectra of Some Tin and Lead Phthalocyanines[1]

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The infrared spectra of $PcSnF_2$, $PcSnCl_2$, $PcSnBr_2$, $PcSnI_2$, $PcSn(OH)_2$, PcSn, α-Pc_2Sn, β-Pc_2Sn, and PcPb are presented in the 286 to 5000 cm.$^{-1}$ region. An interpretation of some features of these spectra is offered.

Introduction

The infrared spectra of phthalocyanines containing Mg, Fe, Co, Ni, Cu, and Zn recently have been investigated over a wide range by Sidorov and Kotlyar.[2] They confirmed earlier observations that polymorphic modifications of the phthalocyanines can be distinguished by their infrared spectra and showed that certain characteristic bands are shifted by amounts ranging up to 55 cm.$^{-1}$ as one central element is exchanged for another. The present work complements the previous infrared studies of phthalocyanines by giving the spectra of one lead and a number of tin phthalocyanines[3-5] over the 286–5000 cm.$^{-1}$ range. These new spectra are discussed in the light of previous spectra and where appropriate in terms of the factors introduced by the presence of tetravalent tin.

Experimental

The infrared spectra were recorded with a Perkin-Elmer Model 221 spectrophotometer. Both the KBr disk and Nujol mull techniques were used with each of the compounds. No evidence of band shifting caused by the use of KBr disks was detected. Figure 1 shows the KBr spectra and Table I gives the frequencies obtained from these spectra.

Discussion

It is reasonable to infer from the structures known for other divalent metal phthalocyanines that both the PcSn and PcPb molecules are planar and possess approximately D_{4h} symmetry. Certainly the similarity of the infrared spectra of these two compounds is consistent with a structural similarity for the molecules. In the event that both have the usual divalent metal phthalocyanine structure, the dissimilarity of the X-ray powder patterns of the two[5] requires that the molecules be packed differently. Simple steric arguments in the case of $PcSn(OH)_2$ and the $PcSnX_2$ series (X = halogen) together with the characteristic phthalocyanino nature of the spectra suggest that these molecules contain octahedrally coordinated tin and accordingly that they all have approximately D_{4h} symmetry (ignoring the hydroxyl hydrogens of $PcSn(OH)_2$). This correlates with previous conclusions.[3,5]

The infrared spectra of the α and β polymorphs of Pc_2Sn and the 1-chloronaphthalene solvate are all very similar. However, the β form is differentiated from the α form by the presence of a small 1041 cm.$^{-1}$ band and the solvate from both the α and β forms by small bands at 970, 791, and 766 cm.$^{-1}$. As in the PcSn–PcPb case, the similarity of the infrared spectra of the polymorphs and the dissimilarity of their X-ray powder patterns[5] suggests that the Pc_2Sn molecules have the same configuration in both cases but are packed differently.

The spectra of the two forms of Pc_2Sn are similar to those of ordinary phthalocyanines except that the 1500 cm.$^{-1}$ region is more complicated. This observation suggests that the rings are not greatly distorted in this unusual compound. Accordingly, the cubic (D_{4h}) or square antiprismatic (D_{4d}) structures discussed by Fernelius[6] appear to be reasonable. Other structures which do not involve considerable distortion of the ring are also possible, of course. If the choice is between the D_{4d} and D_{4h} arrangements and if this structural variation is not the cause of the polymorphism, then the D_{4d} structure is favored, both because of its

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[1] This work was supported by National Science Foundation Grant NSF-G15833. The work was presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962. It is based on portions of the Ph.D. thesis of W. J. K., University Microfilms No. 64-13. Pc = phthalocyanino ligand, $C_{32}H_{16}N_8$.

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