choice of $q = 1.0$, the charge on one end of an oxalate ion, the electrostatic contribution to the activation energy is +25 kcal/mole. The electrostatic contribution to the activation energy will be counterbalanced by an increase in crystal field stabilization energy (CFSE)[6,15] on forming a trigonal-prismatic structure such as E in Figure 1. Fay and Piper[15] estimated this quantity to be between 21 and 30 kcal/mole^{-1} for the tris(trifluoroacetylacetonato)cobalt(III) complex. We have estimated the increase in CFSE for the $[Co(C_2O_4)_3]^{3-}$ ion to be approximately 54 kcal/mole^{-1}.[6] Even with a considerable loss of CFSE in the distortion of the rigid trigonal prism, as suggested by Fay and Piper, the gain in CFSE will very nearly compensate for the increase in electrostatic repulsion and the net activation energy would be expected to be very small. The unusually small activation energy observed for the racemization of $[Co(C_2O_4)_3]^{3-}$ in the solid state is certainly consistent with a trigonal-prismatic activated complex of structure E or F in Figure 1. It is, however, not possible to distinguish between these two choices since the more rigid structure will have a greater CFSE and also a greater electrostatic energy of activation than the distorted structure. The energy difference between structure E and a distorted structure similar to F would therefore probably not be large.

Finally, the very small frequency factor observed in this reaction may be accounted for by the same argument advanced by Ray and Dutt.[14] This argument suggests that the activation energy can be readily lost by an ion through deactivation before it has found its way into the rather improbable twisting motion required for racemization. This would lead to a low probability for passage through the transition state and hence a small frequency factor.

In summary, the experimental evidence presented here is consistent with a trigonal-prismatic activated complex being responsible for the solid-state racemization of $K_3[Co(C_2O_4)_3]\cdot xH_2O$. A stronger claim for support of this mechanism is made difficult, however, by problems inherent in the interpretation of results obtained from kinetic measurements on solid-state reactions. In addition to the uncertainty associated with the interpretation of the effect of waters of hydration on the rate of racemization, it should be pointed out also that lattice distortions over large distances, which may accompany local volume changes in the complex ion, make it difficult to interpret volumes of activation in terms of volume changes of the complex ion alone.[17]

Acknowledgment.—The support of the National Science Foundation is gratefully acknowledged.

[17] The authors wish to thank a referee for drawing our attention to the limitations in interpreting solid-state kinetic results because of unknown lattice effects.

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Tetraphenyldiphosphine Complexes of Nickel(II) and Cobalt(II)

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The ligands 1,4-bis(diphenylphosphino)butane (PC_4P), 1,5-bis(diphenylphosphino)pentane (PC_5P), and bis(diphenylphosphinoethyl) oxide (POP) form complexes of the general formula $M(PC_nP)X_2$ and $M(POP)X_2$ with the halides and thiocyanates of nickel(II) and cobalt(II). All of the ligands are bidentate and complexes with tetrahedral or planar stereochemistry are obtained depending on the nature of the anion.

Introduction

Many complexes of ditertiary diphosphines with the formula $M(ligand)X_2$, where ligand = $R_2P-(CH_2)_n-PR_2$ and X = halogen or NCS, have been prepared and characterized.[1-3] When R is a cyclohexyl group and M = Co(II), the complexes are generally tetrahedral;[4,5] when M = Ni(II), the complexes formed are planar and independent of the length of the chain and of the nature of the ligand X. The complexes with $n = 2$ or 3 are *cis* planar while those with $n = 5$ are *trans* planar.[4] When R = phenyl the complexes are *cis* planar if $n = 1$ or 2 presumably both in the solid state and in solution;[1,2] if $n = 3$ the complexes are planar in the solid state but give rise to an equilibrium of planar and tetrahedral forms in solution.[3] However if a donor atom like sulfur is introduced into the alkyl chain forming, for example, the potentially tridentate ligand $(C_6H_5)_2P(CH_2)_2S(CH_2)_2P(C_6H_5)_2$ (PSP), the ligand behaves as tridentate and forms the pentacoordinated complex $Ni(PSP)I_2$[6] which has been reported to dissociate partially in solution to form planar species.

In order to study the effect of lengthening the alkyl chain and of introducing an oxygen atom into it, of the donor ability of these ligands, and thus of the stereochemistry of the metal complexes formed from them

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[1] G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 1 (1964), and references therein.
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[3] G. R. Van Hecke and W. D. Horrocks, *Inorg. Chem.*, **5**, 1968 (1966).
[4] K. Issleib and G. Schwager, *Z. Anorg. Allgem. Chem.*, **311**, 83 (1961).
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[6] G. Schwarzenbach, *Helv. Chim. Acta*, **49**, 1927 (1966).

TABLE I

ANALYTICAL AND PHYSICAL DATA FOR THE NICKEL(II) AND COBALT(II) COMPLEXES

Compound	Color	Analyses, %										Molar conductivity, cm²/ohm mol[c]	i[d]
		C		H		P		N		Q			
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
$Ni(PC_4P)Br_2$	Dark green	51.37	51.48	4.15	4.16	9.61	9.73			9.10	8.75[a]		
$Ni(PC_4P)(NCS)_2$	Brick red	59.92	60.20	4.70	4.80	10.30	10.29	4.66	4.68	9.76	9.53[a]		
$Ni(PC_5P)Br_2$	Dark green	52.85	52.83	4.59	4.70					8.91	8.86[a]		
$Ni(PC_5P)I_2$	Maroon	46.26	46.60	4.02	4.18	8.23	8.44						
$Ni(POP)Cl_2$	Amethyst	58.78	58.99	4.93	5.30	10.83	10.88			12.40	12.61[b]	0.67	
$Ni(POP)Br_2$	Brown	50.88	50.81	4.27	4.33	9.37	9.50			8.88	9.06[a]	0.25	
$Ni(POP)I_2$	Brown	44.54	45.11	3.74	4.20	8.20	8.35			7.77	7.67[a]	0.57	0.96
$Ni(POP)(NCS)_2$	Brown	58.36	58.20	4.57	4.82			4.54	4.32	9.51	9.64[a]	0.11	
$Co(PC_4P)Br_2$	Sky blue	52.12	52.48	4.37	4.60					9.13	9.00[a]		
$Co(PC_4P)(NCS)_2$	Emerald green	59.90	59.98	4.69	4.65	10.30	10.29	4.66	4.48				
$Co(PC_5P)Br_2$	Turquoise	52.83	53.20	4.59	4.90					8.94	8.80[a]		
$Co(POP)Cl_2$	Blue	58.76	59.13	4.93	5.27	10.82	10.80			12.40	12.60[a]	0.10	
$Co(POP)Br_2$	Blue	50.86	50.11	4.27	4.25	9.37	9.08					0.24	
$Co(POP)I_2$	Emerald green	44.53	44.90	3.74	3.92	8.20	8.40			7.80	7.80[a]	0.39	1.0
$Co(POP)(NCS)_2$	Emerald green	58.35	58.27	4.57	4.72	10.03	10.03	4.53	4.42			0.14	0.98

[a] Q = M. [b] Q = Cl. [c] The molar conductance of $[(C_4H_9)_4N]Br$ in 10^{-3} *M* solution in 1,2-dichloroethane at 25° is 17 cm²/ohm mol. [d] van't Hoff coefficients for *ca.* 5×10^{-3} *M* solution at 37°.

with Ni(II) and Co(II), we have prepared the ligands 1,4-bis(diphenylphosphino)butane, $(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2$ (PC_4P), 1,5-bis(diphenylphosphino)pentane, $(C_6H_5)_2P(CH_2)_5P(C_6H_5)_2$ (PC_5P), and the bis(2-diphenylphosphinoethyl) oxide, $(C_6H_5)_2P(CH_2)_2O(CH_2)_2P(C_6H_5)_2$ (POP). With these ligands metal complexes of the general formula $M(ligand)X_2$ with M = Ni or Co and X = Cl, Br, I, or NCS have been obtained. They have been characterized by magnetic, spectrophotometric, molecular weight, and electrical conductivity measurements.

Experimental Section

Preparation of the Ligands.—The ligands were prepared using the following general method. To 0.05 mol of $(C_6H_5)_2PK \cdot 2(dioxane)$ in 100 ml of anhydrous THF, 0.025 mol of the appropriate ω,ω'-dihaloalkane or bis(2-chloroethyl) oxide dissolved in 30 ml of THF was slowly added while the mixture was stirred. After heating under reflux for about 0.5 hr the solution was concentrated to a small volume. The filtered residue was redissolved in 150 ml of boiling 1-butanol and then filtered and concentrated.

The 1,4-bis(diphenylphosphino)butane was obtained as a colorless crystalline compound, mp 137–139°. *Anal.* Calcd for $C_{28}H_{28}P_2$: C, 78.85; H, 6.62. Found: C, 78.94; H, 6.65.

For the other two ligands the solution was concentrated under vacuum using a steam bath until a clear yellow dense oil was obtained. These oils were used for the preparation of the complexes without further purification.

General Preparation of the Complexes.—To a solution of 5 mmol of the appropriate metal salt in 50 ml of 1-butanol was added the stoichiometric quantity of the appropriate pure ligand (or in the case of the crude ligands, a quantity in slight excess) dissolved in about 50 ml of anhydrous 1-butanol. The solution was concentrated until crystallization began. The crystalline complexes were filtered, washed with cold butanol and petroleum ether (bp 40–70°), and dried in a vacuum oven at 70°.

Physical Measurements.—The absorption spectra were reorded in the range 5000–30,000 cm^{-1} with a Beckman DK2 spectrophotometer and 1-cm silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment with magnesium oxide as the reference.

The conductivity values were measured on a WTW Model LBR/B conductance bridge. The concentration of the solutions in 1,2-dichloroethane was approximately 10^{-2} *M*.

Molecular weights were determined in 1,2-dichloroethane at 37° with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. The concentration of the solutions was approximately 2×10^{-2} *M*. The results were reproducible to ±1%.

The apparatus and the experimental technique used for the magnetic measurements have been described in a previous paper.[7] The Gouy tube was calibrated with freshly distilled water and nickel chloride solution.[8] Diamagnetic corrections were calculated from Pascal's constants.[9]

Results

The complexes are crystalline and stable in air. The analytical data and some physical measurements of the complexes are reported in Table I. The magnetic measurements were made on the solid compounds, and the results are reported in Table II. All of the complexes, with the exception of the nickel thiocyanate complex, are of the high-spin type. The spectra of the solid compounds were all recorded and the positions of the maxima are reported in Table III. Spectrophotometric, conductivity, and molecular weight measurements in solution were taken for only the POP derivatives, PC_nP compounds being too sparingly soluble to allow solution measurements. The diffuse reflectance spectra and the absorption spectra in dichloroethane are practically identical for all of the POP complexes. The

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[7] L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

[8] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 415 ff.

[9] See ref 8, p 403.

TABLE II

MAGNETIC DATA FOR THE NICKEL(II) AND COBALT(II) COMPLEXES

Compound	Temp, °C	$10^6\chi_g$, cgs units	$10^6\chi_M$, cgs units	μ_{eff}, BM
$Ni(PC_4P)Br_2$	21	6.58	4595	3.30
$Ni(PC_4P)(NCS)_2$	22			Diamagnetic
$Ni(PC_5P)Br_2$	20	6.32	4530	3.28
$Ni(PC_5P)I_2$	20	5.37	4434	3.24
$Ni(POP)Cl_2$	21	7.27	4478	3.26
$Ni(POP)Br_2$	22	6.10	4369	3.23
$Ni(POP)I_2$	22	5.34	4401	3.24
$Ni(POP)(NCS)_2$	21			Diamagnetic
$Co(PC_4P)Br_2$	22	12.64	8507	4.50
$Co(PC_4P)(NCS)_2$	18	14.09	8830	4.56
$Co(PC_5P)Br_2$	22	12.87	8846	4.59
$Co(POP)Cl_2$	22	14.32	8512	4.50
$Co(POP)Br_2$	22	14.59	8639	4.55
$Co(POP)I_2$	22	11.32	8918	4.61
$Co(POP)(NCS)_2$	22	12.65	8152	4.41

conductivity measurements in 1,2-dichloroethane and nitroethane show that these complexes are essentially nonelectrolytes. The values of the molecular weight measurements in dichloroethane are within 5% of the values calculated for the monomeric formula.

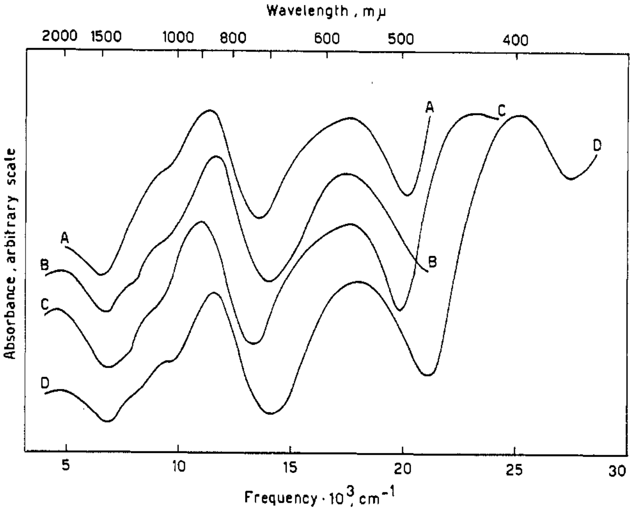

Figure 1.—Diffuse reflectance spectra of: A, $Ni(PC_5P)Br_2$; B, $Ni(POP)Br_2$; C, $Ni(P(C_6H_5)_3)_2Cl_2$; D, $Ni(POP)Cl_2$.

TABLE III

SPECTROSCOPIC DATA FOR THE NICKEL(II) AND COBALT(II) COMPLEXES

Compound	State	Absorption max, cm^{-1} (ϵ_{molar} for soln)
$Ni(PC_4P)Br_2$	Solid	5000, 8900 sh, 11,600, 17,700, 24,400
$Ni(PC_4P)(NCS)_2$	Solid	20,000 sh, 25,200
$Ni(PC_5P)Br_2$	Solid	5000, 8900 sh, 11,200, 17,500, 24,000
$Ni(PC_5P)I_2$	Solid	5000, 8400, sh, 10,800, 17,300 sh
$Ni(POP)Cl_2$	Solid	4900, 8100, 9350, 11,700, 18,200, 24,700
	$(CH_2Cl)_2$	6000 (28), 8100 sh, 9500, 11,700 (133), 18,700 (127), 25,700 (5660)
$Ni(POP)Br_2$	Solid	5000 sh, 8900 sh, 11,600, 17,650
	$(CH_2Cl)_2$	5000, 8800 sh, 11,500 (245), 17,900 (158), 21,750 (5650)
	CH_3NO_2	5000 (36), 8800 sh, 11,500 (200), 17,400 (147), 21,750 (2720)
$Ni(POP)I_2$	Solid	5000, 8000 sh, 11,250, 15,400 sh, 22,200
	$(CH_2Cl)_2$	5000, 10,900 (565), 15,400 sh, 22,650 (4560)
$Ni(POP)(NCS)_2$	Solid	20,000 sh, 25,600
$Co(PC_4P)Br_2$	Solid	6700 sh, 8000, 10,800, 15,000, 16,000, 18,600 sh, 20,400 sh
$Co(PC_4P)(NCS)_2$	Solid	7100, 8900, 11,400, 14,000, 15,600, 16,900, 26,000
$Co(PC_5P)Br_2$	Solid	6700 sh, 7800, 10,500, 15,000, 15,900, 18,400 sh, 20,400 sh
$Co(POP)Cl_2$	Solid	6400, 7500, 9350 sh, 13,700, 15,900
	$(CH_2Cl)_2$	6400 (105), 7600 (80), 9400 sh, 13,650 (374), 15,950 (730), 16,500 sh, 22,750 sh
	CH_3NO_2	6400 (113), 7600 (86), 9400 sh, 13,600 (345), 15,950 (710), 16,500 sh, 22,750 sh
$Co(POP)Br_2$	Solid	6450, 7400, 9350 sh, 14,300 sh, 15,630, 22,200 sh
	$(CH_2Cl)_2$	6450 (126), 7400 (108), 9350 (81), 13,600 (558), 15,650 (920), 22,100 sh
	CH_3NO_2	6300 (115), 7300 (106), 9350 sh, 13,500 (476), 15,200 (857), 21,750 sh
$Co(POP)I_2$	Solid	5900 sh, 7250, 8500 sh, 14,800
	$(CH_2Cl)_2$	6100 sh, 7300 (120), 8800 (106), 12,800 (176), 14,800 (745)
$Co(POP)(NCS)_2$	Solid	7150, 8650, 10,600, 15,600, 16,500, 25,000
	$(CH_2Cl)_2$	7400 sh, 8500 (207), 10,000 sh, 16,200 (860), 17,000 sh, 27,050 (5500)

Discussion

Nickel Halide Complexes.—The spectra of all of these complexes, compared in the solid state and in solution, are very similar (Figure 1). The small displacements observed for the absorption maxima of the complexes with the same ligand and different halogen vary according to the relative position of the halogens in the spectrochemical and nephelauxetic series. Therefore all of the complexes, those of the POP and PC_nP derivatives, may be assigned the same stereochemistry around the metal ion. The spectra show an absorption maxima at about 4500 cm^{-1}, a large asymmetric band whose maximum is about 11,000 cm^{-1} with shoulders toward the lower frequency part of the band, and another band at about 17,000 cm^{-1}. The high intensity of the bands (ε 100–200) is indicative of a configuation which is not centrosymmetric. The spectra are very similar to those of the complex $Ni(P(C_6H_5)_3)_2Cl_2$[10] which has been shown to have a pseudo-tetrahedral structure by X-ray crystal structure analysis.[11] These spectrophotometric data and the magnetic moments lead us to conclude that the metal has a pseudo-tetrahedral coordination with the set of donor atoms P_2X_2. The fact that the complexes of POP are monomeric

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(11) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *ibid.*, 3625 (1965).

and that their crystal field spectra are practically identical with those of PC_nP indicate that the oxygen atom of the POP ligand is not coordinated to the metal ion. Because of their insolubility it cannot be excluded that the PC_nP complexes achieve tetrahedral coordination by bridging of diphosphine between two metal ions. By analogy with the spectra of $Ni(P(C_6H_5)_3)_2X_2$ and other NiL_2X_2 complexes, the band occurring at 17,000 cm^{-1} is assigned to the ν_3 transition $^3T_1(F) \rightarrow {}^3T_1(P)$ and the band at about 12,000 cm^{-1} to the ν_2 transition $^3T_1(F) \rightarrow {}^3A_2(F)$ in the symmetry field T_d. The band at 4500 cm^{-1} and the shoulders of the 12,000-cm^{-1} band have been assigned to the components of the ν_1 transition $^3T_1(F) \rightarrow {}^3T_2(F)$, which is triply degenerate in symmetry T_d. The large splitting of the level $^3T_2(F)$ is indicative of a strong distortion from T_d symmetry.[12] This is also confirmed by the relatively low values of the μ_{eff} which range from 3.20 to 3.30 BM indicating a low orbital contribution.

Nickel Thiocyanate Complexes.—These complexes are diamagnetic and their spectra do not show absorption below 16,000 cm^{-1}. Therefore they have been assigned an essentially square-planar structure. Their low solubility in organic solvents does not allow dipole moment measurements to be performed, and thus no conclusion can be made as to whether the complexes have *cis-* or *trans-*planar structure. It is interesting to note that all of the thiocyanate complexes of nickel with phosphines are planar even if the corresponding halogen compounds are pseudo-tetrahedral.[10,13] This may be explained by the high donor power of the nitrogen of the thiocyanate group which is capable of inducing a singlet ground state in all cases.

These results indicate that the complexes $Ni(PC_nP)X_2$ with $n = 4$ or 5 are similar to the bis-triphenylphosphino analogs. All of the halogen complexes are of the high-spin type in the solid state and in solution, while the thiocyanate complexes are of the low-spin type and form square-planar structures. The PC_nP derivatives with $n = 2$ or 3, on the other hand, are all planar in the solid state.[2,3] The electronic factors apparently are not as important for the variation of structure as the different values for n. Presumably increasing the length of the chain causes a larger crowding around the nickel atom in such a manner that the achievement of a square configuration becomes unfavorable. It is interesting to note that while the $Ni(PSP)I_2$ complex[6] is pentacoordinated with the sulfur bonded to the metal, the POP analogs are pseudo-tetrahedral with the oxygen atom remaining unbonded. This may be attributed to the difference in donor power of the two atoms of the sixth group. However an atom of oxygen which is found in a similar position in the ligand bis(2-dimethylaminoethyl) oxide (daeo) binds to the bivalent 3d metal ion forming pentacoordinated complexes of the formula $Ni(daeo)X_2$.[14] It is difficult to explain the different behavior of the ethereal oxygen atom in the two ligands POP and daeo. It is possible that the larger size of the diphenylphosphino group in comparison to that of the dimethylamine forces its atoms to form a chelate ring in such a way that the oxygen atom is at a greater distance from the metal in the POP complexes. Also it cannot be excluded that a very weak metal to oxygen interaction compared with a strong metal to phosphorus interaction causes only a negligible effect on the crystal field energies of the metal ion.

Cobalt Complexes.—The cobalt complexes exhibit very similar spectra with all of the ligands. One very intense band with three maxima is present in the range 6000–10,000 cm^{-1}, and another band generally resolved into two peaks and a shoulder occurs in the range 15,000–18,000 cm^{-1} (Figure 2). These spectra are very similar to those of the pseudo-tetrahedral complexes $Co(P(C_6H_5)_3)_2X_2$[15] as well as to those of all of the pseudo-tetrahedral complexes of Co(II).[12] The bands have therefore been assigned to the transitions ν_2 $[{}^4A_2(F) \rightarrow {}^4T_1(F)]$ and $\nu_3[{}^4A_2(F) \rightarrow {}^4T_1(P)]$ in a field of symmetry T_d. The large splitting of each of these bands is caused by strong distortion of these complexes which removes the triple degeneracy of the terms. The magnetic moments range from 4.40 to 4.60 BM. The orbital contribution is small as is generally found for tetrahedral complexes.[16] Because of the instability of the PC_nP cobalt complexes, a polymeric structure, by analogy with the nickel halide compounds, cannot be ruled out.

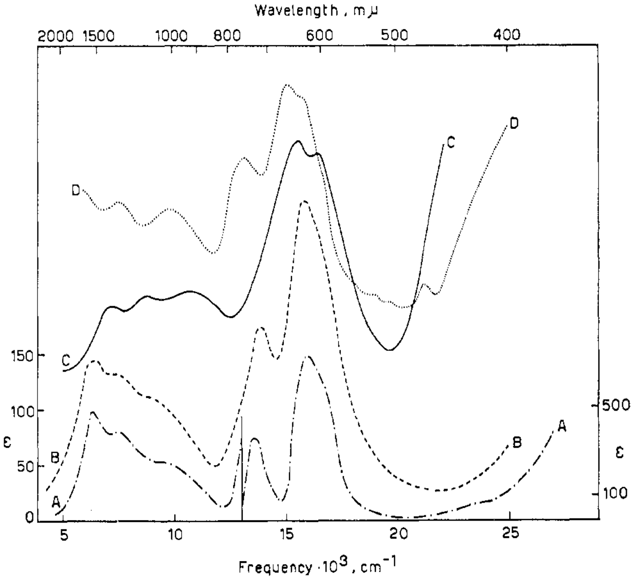

Figure 2.—Absorption spectrum in $(CH_2Cl)_2$ solution of: A, $Co(POP)Cl_2$. Diffuse reflectance spectra of: B, $Co(POP)Cl_2$; C, $Co(POP)(NCS)_2$; D, $Co(P(C_6H_5)_3)_2Br_2$.

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