Contribution from the Richardson Chemistry Laboratory of Tulane University, New Orleans, Louisiana

Nickel (II) and Cobalt (II) Complexes of *cis* - 1,2, bis (Diphenylphosphino) Ethylene*

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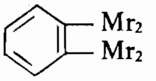
*Nickel(II) and cobalt(II) complexes with 1,2-*cis* (diphenylphosphino) ethylene are reported. Magnetic susceptibility, infrared and visible spectra, and conductivity studies have been made. The existence of a spin-free spin-paired equilibrium is proposed for the nickel(II) nitrate complex. The magnetic properties and infrared data are discussed in terms of possible structures for the complexes. The magnetic moments of the nickel(II) complexes are intermediate between the values expected from a diamagnetic and paramagnetic species. The moment for the cobalt(II) complexes are normal for a specie with one unpaired electron. The infrared spectra of the complexes do not show the presence of coordinated nitrate or perchlorate anions. However, the appearance of the C=C stretching absorption, which is infrared inactive for the uncomplexed, symmetrical ligand indicates that some asymmetry exists about the double bond in the solid complexes.*

Introduction

Several transition metal complexes of orthophenylenebis(disubstituted phosphines and arsines) (I) have been reported in the literature.[1,2,3]

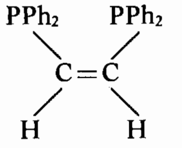


M = As, P
r = alkyl or aryl

(I)

These ligands are excellent donors with π bonding ability due to low-lying d orbitals. In many cases the cationic chelates can be reduced to zero valent metal complexes.

Recently Sacco[4] and W.D. Horrocks[5,6] reported several complexes of the type $[Co(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_mX_2$ where n=1,2,3 and m=1,2. They assigned pentacoordination to compounds containing anions like Cl^-, Br^-, NO_3^- etc., with C_{2v} symmetry on the basis of epr and spectral data.[6]



(abbrv. VPP)

(II)

We wish to report here the preparation of some nickel(II) and cobalt(II) chelates of *cis*-1,2-bis(diphenylphosphino) ethylene as well as their spectral and magnetic properties which bear on the structure of these complexes.

Experimental Section

The ligand was prepared according to the procedure given by Aguiar and Daigle.[7]

The respective metal salt solutions in acetone were slowly added with constant stirring to hot ethanol solutions of the ligand in a 1:2 molar ratio. An immediate intense color change occurred. The deeply colored complexes precipitated on cooling. The precipitates were filtered and washed several times with acetone and dried over anhydrous calcium chloride in a desiccator. All the complexes are insoluble in non-polar but soluble in polar organic solvents.

Analytical Data. Bis *cis*-1,2 bis(diphenylphosphino) ethylene nickel(II) nitrate, $[NiP_4C_{52}H_{44}](NO_3)_2$. Calcd. C, 63.37; H, 4.46; N, 2.84; Ni, 5.96. Found. C, 63.04; H, 4.59; N, 3.06; Ni, 5.59.

Bis *cis*-1,2-bis(diphenylphosphino)ethylene nickel(II) perchlorate, $[NiP_4C_{52}H_{44}](ClO_4)_2$. Calcd. C, 58.56; H, 4.21; Cl, 6.77; P, 11.77. Found. C, 58.78; H, 4.49; Cl, 6.07; P, 11.02.

Bis *cis*-1,2 bis(diphenylphosphino)ethylene cobalt(II) nitrate, $[CoP_4C_{52}H_{44}](NO_3)_2$. Calcd. C, 63.81; H, 4.49; Co, 6.02. Found. C, 63.51; H, 4.82; Co, 6.38.

Bis *cis*-1,2 bis(diphenylphosphino)ethylene cobalt(II) perchlorate, $[CoP_4C_{52}H_{44}](ClO_4)_2$. Calcd. C, 59.43; H, 4.19; Cl, 6.75. Found. C, 59.01; H, 4.37; Cl, 6.07. Some of the physical properties of these complexes are listed in Table I.

(*) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1965.

(1) J. Chatt, F. A. Hart and H. R. Watson, *J. Chem. Soc.*, 2537 (1962).

(2) K. Issleib and C. Schwager, *Z. Anorg. Chem.*, *83*, 311 (1961).

(3) G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).

(4) A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, *93*, 687 (1963).

(5) G. R. Van Hecke and W. D. Horrocks Jr., *Inorg. Chem.*, *5*, 1960 (1966).

(6) W. D. Horrocks Jr., G. R. Van Hecke and D. D. Hal, *Inorg. Chem.*, *6*, 694 (1967).

(7) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, *86*, 2299 (1964).

Table I. Color, Melting Point, Magnetic Moment of the Complexes

Complex	Color	M.P. (°C)	T (°K)	χ_g $\chi_{10^{-6}}$	χ_M $\chi_{10^{-6}}$	χ_{dia} $\chi_{10^{-6}}$	μ_{eff}
$Co(Ph_2PCH=CHPPh_2)_2(NO_3)_2$	Brown	180 (decomp)	300	1.503	1.459	493	2.15
$Co(Ph_2PCH=CHPPh_2)_2(ClO_4)_2$	Yellow	265	300	2.410	2.523	513	2.65
$Ni(Ph_2PCH=CHPPh_2)_2(NO_3)_2$	Yellow	200	298	0.820	793	493	1.67
$Ni(Ph_2PCH=CHPPh_2)_2(ClO_4)_2$	Yellow	286 (decomp)	299	0.410	430	513	1.50

Magnetic Susceptibility Measurements. Magnetic measurements were made by the standard Gouy technique. The diamagnetic corrections were calculated from Pascal's constants. The effective magnetic moment was calculated from the expression $\mu_{eff} = 2.84 \sqrt{\chi_M^{cor} T}$.

Spectrophotometric Measurements. Infrared absorption spectra were obtained using a Beckman IR-8 recording spectrophotometer. Both nujol mulls and KBr discs were used to obtain the spectra of the complexes. Near infrared and visible spectra of solutions were obtained with a Cary Model-14 spectrophotometer. Reflectance spectra in the same region were obtained on a recording model Beckman DK spectrophotometer using dry LiF as the standard.

Conductivity Measurements. Measurements of the conductivities of nitromethane solutions of the complexes were made using an Industrial Instruments, Inc., Model Rc16B2 conductivity bridge and a cell which was previously calibrated with aqueous KCl solutions.

Results and Discussion

I. *Cobalt(II) Complexes.* The magnetic properties of these complexes indicate that they are square planar in the solid state. Their magnetic moments fall into the range expected for square planar cobalt(II) complexes (2.1-2.9 BM). The two cobalt(II) complexes also follow the Curie-Weiss Law as indicated by magnetic susceptibility measurements at various temperatures. The higher moment for the perchlorate seems to be due to a large orbital contribution. The infrared spectra in KBr and nujol mulls were identical and indicate the ionic character of the nitrate and the perchlorate ions. Bands at 1110 cm^{-1} and 930 cm^{-1} for the perchlorate and at 1380 cm^{-1} for the nitrate indicate that the anions do not coordinate. The IR spectra did not show any bands due to water or other solvents. The conductivity of the complexes were measured at different concentrations. The conductivity of the perchlorate complex does not change appreciably with concentration. The nitrate complexes, however, show some ion-pairing as indicated by the decrease in conductivity as the concentration increases (Table II). These experimental data seem to be in line with the magnetic properties indicative of a square planar structure for the complex with ionic nitrates and perchlorates.

The electronic visible absorption spectra (Table III, Figure 1) do not seem to contradict these conclusions.

II. *Nickel(II) Complexes.* The yellow complex $Ni(VPP)_2(NO_3)_2$ belongs to the interesting group of nickel(II) complexes which show anomalous behavior.[8]

Table II. Conductivity Data

Complex	Concn. M	molar
$[Co(Ph_2PCH=CHPPh_2)_2](NO_3)_2$	1.243×10^{-3}	86
	1.067×10^{-3}	99
	6.292×10^{-4}	107
	5.168×10^{-4}	122
	3.142×10^{-4}	155
$[Co(Ph_2PCH=CHPPh_2)_2](ClO_4)_2$	4.200×10^{-4}	160
	1.312×10^{-3}	165
$[Ni(Ph_2PCH=CHPPh_2)_2](NO_3)_2$	3.770×10^{-3}	134
	3.370×10^{-3}	136
	1.822×10^{-3}	148
	1.054×10^{-3}	156
	1.594×10^{-4}	164
$[Ni(Ph_2PCH=CHPPh_2)_2](ClO_4)_2$	6.400×10^{-4}	180
	4.400×10^{-4}	180

Table III. Electronic Visible Absorption Spectra

Complex	Medium	mμ**
$Co(Ph_2PCH=CHPPh_2)_2(NO_3)_2$	LiF	1100 (v.b.), 450, 350
	Nitromethane	950 (437), 785 (172)
$Co(Ph_2PCH=CHPPh_2)_2(ClO_4)_2$	LiF	900, 700, 460 (sh)
	Nitromethane	1000 (sh), 950 (192), 720 (160), 475 (sh)
$Ni(Ph_2PCH=CHPPh_2)_2(NO_3)_2$	LiF	1060 (w), 445 (sh)
	Nitromethane	930 (782), 430 (2084)
$Ni(Ph_2PCH=CHPPh_2)_2(ClO_4)_2$	LiF	1080 (w), 460 (sh)
	Nitromethane	950 (852), 810 (sh), 435 (2817)

** Numbers in the parenthesis indicate the molar extinction co-efficient calculated at the band maxima; v.b., very broad; sh, shoulder; b, broad; w, weak.

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[8] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 2nd Edition, Interscience, New York, 1966, pp. 886-890.

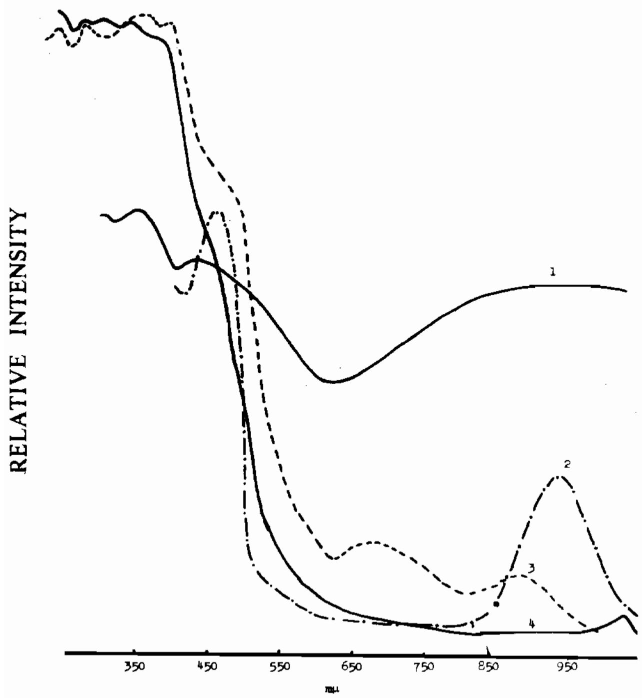

Figure 1. Absorption Spectra of the Complexes.
1. $Co(No_3)_2(UPP)_2$ in LiF. 2. $Ni(NO_3)_2(UPP)_2$ in CH_3NO_2.
3. $Co(ClO_4)_2(UPP)_2$ in LiF. 4. $Ni(ClO_4)_2(UPP)_2$ in LiF.

Magnetic susceptibility measurements indicate an equilibrium between spin-paired and spin-free electronic ground states in the complex. The variation of magnetic moment with temperature (Table IV) indicates that the magnetic property of this complex does not follow the Curie-Weiss Law.

Table IV. Magnetic Susceptibility Data for $Ni(Ph_2PCH=CHPPh_2)_2(NO_3)_2$ Complex

T°K	μ_{eff}	% Paramagnetism[a]	$N_{^1A}$[b]	$N_{^3B}$[b]	K	ΔE[c] (cal/mole)
300	1.67	25	0.75	0.25	0.33	540
320	1.92	34	0.66	0.34	0.51	468
350	2.28	50	0.50	0.50	1.00	330
370	2.50	60	0.40	0.60	1.50	185
398	2.82	77	0.23	0.77	3.34	144
410	2.95	85	0.15	0.85	5.66	negative
421	3.14	96	0.04	0.96	24.00	negative

[a] % Paramagnetism $= \frac{(\mu_{eff})^2}{(3.2)^2} \times 100.$ [b] From $\mu_{eff}^2 = (0.5)^2N_1+(3.2)^2N_3.$ [c] From $\mu_{eff} = 3.2(1+\frac{1}{3^c}-\Delta E/RT)^{-1/2}.$

It is predicted from ligand field theory that the triplet state becomes thermally accessible in the neighborhood of the cross-over point where the energy separation between the singlet and triplet state becomes comparable with ordinary thermal energies. The data (Table IV) provide strong evidence for the existence of a Maxwell-Boltzman distribution of states of different spin-multiplicities. The magnetic moment at room temperature is intermediate between that of the complex in the low-spin state (0.5 B.M. due to residual paramagnetism) and in the high spin state (3.2 B.M.).

The interpretation given by Maki[9] for salicylaldimine nickel(II) complexes was extended by Ballhausen and Liehr[10] who derived an expression to correlate the magnetic susceptibility and absolute temperature for a system having such degenerate electronic ground states. This requires that the energies of the singlet and triplet states are greatly influenced by nonequivalent groups along the Z axis above and below the metal ion which is bound to four donor atoms in the plane. As the axial field decreases the singlet state which lies above the triplet state in an octahedral environment drops in relative energy. When the right relative axial in plane ligand field strength has been reached the singlet and triplet states should be close in relative energies. The configuration for the two states would then be

$$(e_g)^4(b_{2g})^2(a_{1g})^2 \quad \text{low spin}$$
$$(e_g)^4(b_{2g})^2(a_{1g})(a_{1g})^1 \quad \text{high spin}$$

and a thermal transition should now occur.

The equilibrium constant for such a transition

$$^1A \leftrightarrows {}^3B$$
$$\text{spin paired} \leftrightarrows \text{spin free}$$

can be calculated from a knowledge of the mole fraction ($N_{^1A}$ and $N_{^3B}$) of the two species. The mole fractions in them are calculated from the magnetic susceptibilities assuming a moment of 3.2 B.M. for the 100% high-spin species and 0.5 B.M. (residual paramagnetism) for the 100% low spin species (Table IV).

A plot of log K against 1/T gave a straight line within the experimental error. An approximate value of 590 cal/mole (210 cm^{-1}) for ΔH_{300} was calculated from the slope of the straight line. The energy difference (ΔE) between these two electronic ground states is of the order of kT (208 cm^{-1} at 300°K) and relatively small changes in temperature will produce changes in the mole fractions of the singlet and triplet states. The theory of Ballhausen and Liehr[10] predicts that the entropy changes for the equilibrium $^1A \leftrightarrows {}^3B$ should be positive. The entropy change found for the $Ni(VPP)_2(NO_3)_2$ complex in the solid state equals +0.25 eu. This seems to indicate that these entropy changes are produced primarily by changes in spin multiplicity.[11]

The complex $Ni(VPP)_2(ClO_4)_2$ on the other hand, does not show anonalous magnetic behavior. It follows the Curie-Weiss Law as shown by magnetic susceptibility measurements at various temperatures.

This difference in magnetic behavior between nitrates and perchlorates of nickel(II) complexes has been observed previously.[12] It can be attributed to differences in axial perturbance between these two anions. The perchlorate ion with its poor coordinating ability produces little or no axial disturbance and therefore no singlet-triplet transitions. The nitrate ion, on the other

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(9) G. Maki, *J. Chem. Phys.*, *29*, 1129 (1958).

(10) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, *81*, 538 (1959).

(11) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, *86*, 4830 (1964).

(12) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, *616*, 1125 (1963).

hand, with its somewhat greater coordinating ability, would produce an axial disturbance great enough to allow singlet-triplet transitions and non Curie-Weiss Law behavior.

Since greater axial perturbance was indicated for the nitrate ion it was of interest to see if this ion acted as a monodentate ligand. Infrared studies of the complex in KBr and nujol mull, indicated a strong band at 1380 cm^{-1} a band characteristic of an ionic nitrate. For the complex perchlorate bands at 1110 cm^{-1} and 930 cm^{-1} were observed which also are characteristic of ionic perchlorates.

The infrared studies of the solid complexes also revealed a medium band at 1620-1625 cm^{-1} which is assigned to the C=C stretching frequency. The appearance of this band which is inactive for the uncomplexed ligand indicates an asymmetry around the double band in the complexes.

The Raman spectrum of the complex shows similar lines as in the infrared spectrum indicating that a center of symmetry is absent.

The conductivity of the nitrate complexes (Table II) decreases with increase in concentration indicating that some ion-pair formation occurs in concentrated solutions. No such ion-pair formation was observed for the perchlorate complex.

These data seem to indicate that in the solid state for the $[Ni(VPP)_2](NO_3)_2$ complex the ionic nitrate ion produces an axial perturbation along the Z axis. This is the reason for the unusual magnetic behavior of the square planar $[Ni(VPP)_2]^{++}$ ion. No axial perturbations are observed for the $[Ni(VPP)_2](ClO_4)_2$ and the two cobalt(II) complexes reported in this paper.

Single crystal X-ray work on the complex $[Ni(VPP)_2](NO_3)_2$ is in progress.

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