tion number of the palladium changes in this sequence. The effect of oxidation state on binding energy is in complete conformity with data previously published on such trends.[9]

During the course of these studies, we also determined the binding energies of the potassium 2s, bromine 3p, and phosphorus 2p levels and the results are given in Table II. The potassium is present in these compounds as the cation component of the ionic lattice; hence, we expect its inner-shell binding energies to be almost constant unless crystal field effects bring about differences. The observed K(2s) binding energy is constant to within 0.2 eV, which we take as weak evidence that crystal field effects can be ignored.

The data show that there is essentially no difference in the $3p_{3/2}$ level of bromine in the compounds $K_2[PdBr_4]$ and $[Pd(P(C_6H_5)_3)_2)Br_2]$, but the Br $3p_{3/2}$ level of these compounds is about 0.5 eV lower than the Br $3p_{3/2}$ level in $PdBr_2$. We attribute the higher value for $PdBr_2$ to the effect of each bromine being coordinated to two palladium atoms in a bridging structure. This conclusion is supported by the expectation that such bridging-type bonds should result in higher binding energies for the electrons in the bridging atoms as they are coordinated to two close acceptor atoms and thus have lower electron densities than in cases where they are coordinated to only one acceptor atom.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation. We also wish to acknowledge NSF Grant GP5441 used toward the purchase of the Perkin-Elmer 621 spectrometer and NSF Grant GP6932 used toward the purchase of the Cary 81 spectrometer. In addition, we wish to thank Dr. Raymond Frey of Fisk University for assistance in obtaining the Raman spectra.

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Zwitterion Complexes of the Cation Dicyanobis[1,2-bis(diphenylphosphino)ethane]cobalt(III)

BY P. RIGO,* B. LONGATO, AND G. FAVERO

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The cobalt(III) complex $L^+ = [Co\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\}_2(CN)_2]^+$ acts as positively charged ligand giving compounds of the stoichiometry $M(L^+)X_3$, where M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II) and X = halogen or pseudohalogen. On the basis of their electronic and vibrational spectra, magnetic susceptibilities, and X-ray diffraction patterns, these compounds are formulated as pseudotetrahedral zwitterion complexes in which the cobalt(III) cation is bound to MX_3^- moieties through the nitrogen atom of one cyanide group.

Introduction

We have recently reported the preparation of the compound $Co(dpe)_2(CN)_2$ (dpe = $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$) which we formulated as a low-spin five-coordinate complex of cobalt(II) where one of the two diphosphines acts as a monodentate ligand.[1] Methanol solutions of the compound were found to react with oxygen giving the hexacoordinate cobalt(III) species $[Co(dpe)_2(CN)_2]^+$. Investigations have now been extended to the reactions of the complex with oxygen in 1,2-dichloroethane. We find that the reaction yields *inter alia* the compound $Co^{III}(dpe)_2(CN)_2Co^{II}Cl_3$ which can be formulated as a zwitterion made by the cation $[Co^{III}(dpe)_2(CN)_2]^+$ bound through the nitrogen end of one CN group to the Co(II) atom of the $CoCl_3^-$ moiety. Several recent reports have been concerned with zwitterion systems in transition metal complexes containing positively charged nitrogen and phosphorus ligands.[2–9] In the present paper we report the preparation and the characterization of a series of compounds in which the ionic species $[Co(dpe)_2(CN)_2]^+$ acts as a positively charged ligand for MCl_3^- anions. The general composition of the complexes is $M(L^+)X_3$ where $L^+ = [Co(dpe)_2(CN)_2]^+$; M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II); X = halogen or pseudohalogen.

Experimental Section

Apparatus.—The magnetic moments were determined at 25° by using the Gouy method and were corrected for the diamagnetism of the ligands.[10] Electronic spectra were recorded on an Optica CF4NI spectrophotometer. The reflection spectra were measured with a Beckman DU spectrophotometer using solid compounds ground with $MgCO_3$ as the inert diluent. Ir spectra were recorded using a Beckman IR 9 spectrophotometer. Conductivity measurements were made at 25°. X-Ray powdered diffractograms were taken using a Siemens diffractometer, Model F-Nr. The uptake of oxygen was measured as described previously.[11]

Starting Materials.—Metal salts were analytical reagent grade.

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TABLE I

SOME PROPERTIES AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Color	Magnetic moment,[a] μ_{eff}, BM	Analyses, %: C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	X[b] Calcd	X[b] Found
$[Co(dpe)_2(CN)_2]ClO_4$	Yellow	Diamag	64.39	65.04	4.80	4.98	2.78	2.86	3.52	3.52
$[Co(dpe)_2(CN)_2]CoCl_3$	Green	4.45[c]	60.44	59.92	4.51	4.49	2.61	2.60	9.91	9.97
$[Co(dpe)_2(CN)_2]CoBr_3$	Green	4.50[c]	53.76	53.65	4.01	4.10	2.32	2.38	19.87	19.44
$[Co(dpe)_2(CN)_2]Co(NCS)_3$	Green	4.57[c]	60.00	60.25	4.24	4.27	6.13	6.34	. . .	. . .
$[Co(dpe)_2(CN)_2]MnCl_3$	Yellow	5.79[c]	60.67	61.22	4.52	4.68	2.62	2.60	9.95	9.98
$[Co(dpe)_2(CN)_2]FeCl_3$	Green	5.22[c]	60.61	59.03	4.52	4.46	2.61	2.59	9.94	10.22
$[Co(dpe)_2(CN)_2]NiCl_3$	Green	3.78[c]	60.45	59.92	4.51	4.49	2.61	2.67	9.91	10.10
$[Co(dpe)_2(CN)_2]ZnCl_3$	Yellow	Diamag	60.08	59.15	4.48	4.54	2.59	2.76	9.85	10.19

[a] At room temperature. [b] X = halogen. [c] Magnetic moment calculated by considering only one paramagnetic center per molecule.

TABLE II

CONDUCTANCE AND ELECTRONIC SPECTRAL DATA IN THE 14,000–18,000-CM^{-1} REGION FOR SOME COMPLEXES

Complex	Λ_M,[a] cm^2 ohm^{-1} mol^{-1}	Absorption max, cm^{-1}: Solid state	CH$_2$Cl$_2$ soln (ϵ)[b]
$[Co(dpe)_2(CN)_2]ClO_4$	52[c]	*d*	*d*
$Co(dpe)_2(CN)_2CoCl_3$	8.1	14,700	14,600 (495)
		15,150	15,150 (460)
		15,500 sh	15,750 sh (350)
		16,670	16,670 (575)
$Co(dpe)_2(CN)_2CoBr_3$	5.1	14,290	14,270 (770)
		14,600	14,680 (775)
		15,500	15,500 (655)
		15,870	15,950 (560)
$Co(dpe)_2(CN)_2Co(NCS)_3$	1.0	15,750	15,750 (630)
		17,390	17,390 (1125)
$Co(dpe)_2(CN)_2NiCl_3$	*e*	14,550	*e*
		16,660	

[a] Λ_M is molar conductance obtained on approximately 5×10^{-4} *M* dichloromethane solutions. [b] ϵ is molar absorptivity at band maxima in parentheses. [c] $\Lambda_M = 25.2$ in 10^{-3} *M* nitrobenzene solution. [d] No absorption. [e] Investigation limited to solid state.

TABLE III

C≡N STRETCHING FREQUENCIES, IN CM^{-1}, OF THE COMPLEXES[a]

Complex	CN terminal	CN bridging	$\Delta\nu_1$[b]	$\Delta\nu_2$[c]
$Co(dpe)_2(CN)_2ClO_4$	2113	. . .	. . .	. . .
$Co(dpe)_2(CN)_2CoCl_3$	2108	2146	−5	33
$Co(dpe)_2(CN)_2CoBr_3$	2106	2132	−7	19
$Co(dpe)_2(CN)_2Co(NCS)_3$	2112	2148	−1	35
$Co(dpe)_2(CN)_2MnCl_3$	2108	2139	−5	26
$Co(dpe)_2(CN)_2FeCl_3$	2109	2137	−4	24
$Co(dpe)_2(CN)_2NiCl_3$	2108	2152	−5	39
$Co(dpe)_2(CN)_2ZnCl_3$	2107	2151	−6	38

[a] In Nujol mulls. [b] $\Delta\nu_1 = \nu(CN)(\text{terminal}) - \nu(CN)$(in the free ion $[Co(dpe)_2(CN)_2]^+$). [c] $\Delta\nu_2 = \nu(CN)(\text{bridging}) - \nu(CN)$ (in the free ion $[Co(dpe)_2(CN)_2]^+$).

1,2-Bis(diphenylphosphino)ethane was prepared by standard methods of the literature.[12]

Preparation of the Complexes.—Some properties and analytical data for the complexes are reported in Tables I–III.

$Co(dpe)_2(CN)_2$.—$[Co(dpe)_2Br]Br$[13] (4 mmol) and the ligand dpe (2 mmol) were dissolved in 100 ml of 8:2 ethanol–methylene chloride. The green solution was passed through a column of an anionic resin (Dowex 1-X4, 50–100 mesh) in CN$^-$ form. The resulting red solution was evaporated to dryness and the red crystals were washed several times with ether and dried *in vacuo*. The complex is air sensitive and was prepared in a nitrogen atmosphere.

$[Co(dpe)_2(CN)_2]ClO_4$.—The complex $Co(dpe)_2(CN)_2$ (1 mmol) suspended in 50 ml of methanol at 25° rapidly absorbed 0.5 mmol of O_2 giving an orange-red solution. Upon addition of a concentrated solution of $NaClO_4$ in methanol, yellow crystals were obtained which analyzed as $[CO(dpe)_2(CN)_2]ClO_4$. This product was recrystallized from methylene chloride–methanol.

$[Co(dpe)_2(CN)_2]CoCl_3$.—The compound $Co(dpe)_2(CN)_2$ (1 mmol) suspended in 25 ml of 1,2-dichloroethane rapidly absorbed 0.5 mmol of O_2 giving an orange-red solution. This absorption step was followed by a slower uptake of oxygen and the solution turned green. The green crystals which separated on standing (2 days) were collected, washed with dichloroethane, and purified by dissolving in methanol and adding ether.

$[Co(dpe)_2(CN)_2]CoX_3$ (X = Cl, Br, NCS).—A solution of $[Co(dpe)_2(CN)_2]ClO_4$ (1 mmol) and CoX_2 (1 mmol) in hot methanol gave green crystals when treated with an excess of LiX (X = Cl, Br). The chloro and bromo complexes were purified by dissolving in methanol and adding ether. The thiocyanato complex was prepared using NaNCS and purified by crystallization from CH_2Cl_2–C_2H_5OH.

$[Co(dpe)_2(CN)_2]MCl_3$ (M = Mn, Fe, Ni, Zn).—$[Co(dpe)_2(CN)_2]ClO_4$ (1 mmol) in 25 ml of dichloromethane was added to a solution of MCl_2 (1 mmol) and LiCl (1 mmol) in 50 ml of 1-butanol. The resulting solution was concentrated and the product obtained was recrystallized by dissolving in methanol and adding ether. The iron(II) complex which is air sensitive was prepared in a nitrogen atmosphere.

Results and Discussion

The Complexes $[Co(dpe)_2(CN)_2]^+$ and $[Co(dpe)_2(CN)_2]CoCl_3$.—The reaction of the cobalt(II) complex $Co(dpe)_2(CN)_2$ with oxygen in methanol containing $NaClO_4$ yields a yellow solid which analyzes as $Co(dpe)_2(CN)_2ClO_4$. The compound is diamagnetic. The values of the conductance in nitrobenzene and CH_2Cl_2 solutions are typical of uni-univalent electrolytes (Table II). The infrared spectrum shows one sharp band at 2113 cm^{-1} attributable to the stretching of CN groups in the trans position and a single broad peak in the perchlorate stretching region at 1080 cm^{-1}. The absence of splitting of this band rules out the possibility of perchlorate coordination.[14] These facts coupled with the conductance and magnetic properties show that the compound is the perchlorate of the six-coordinate Co(III) complex $[Co(dpe)_2(CN)_2]^+$ in which the cyanide groups are in trans positions.

Manometric measurements showed that the oxidation of 2 mol of cobalt(II) to cobalt(III) complexes involved the uptake of 1 mol of oxygen. This fact indicates that a binuclear peroxo complex is probably formed,[1] which we were unable to isolate. When the reaction was carried out in dichloroethane, the formation of the oxygen adduct was followed by a further slow uptake of oxygen and simultaneous evolution of CO_2. This second step involved also dehalogenation of the dichloroethane and formation of a cobalt complex containing chlorine which analyzed as $Co_2(dpe)_2(CN)_2Cl_3$. The magnetic moment of about 3.2 BM/formula weight suggests the presence of one cobalt(III)

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in low-spin configuration and one cobalt(II) in high-spin configuration. Indeed the magnetic moment calculated by considering only one paramagnetic center per molecule gives the value 4.50 BM which is within the range usually observed for tetrahedrally coordinated high-spin complexes.[10]

The complex is virtually insoluble in nonpolar organic solvents and is decomposed by water and other strong-donor solvents. It changes coordination on going from solid to methanolic solutions as is qualitatively indicated by the change in color from green in the solid to yellow in solution. Treatment of these yellow solutions with $NaClO_4$ yields a yellow compound which was identified as the cobalt(III) complex $[Co(dpe)_2(CN)_2]ClO_4$ by means of elemental analysis and infrared spectroscopy.

Dichloromethane appears to be the only solvent in which the complex $Co_2(dpe)_2(CN)_2Cl_3$ dissolves without chemical changes. The visible spectra in CH_2Cl_2 and the reflectance spectra are very similar and show a broad multicomponent band in the 14,000–18,000-cm^{-1} region where the cation $[Co(dpe)_2(CN)_2]^+$ does not absorb. The spectrum is very similar to, but not identical with, that of the four-coordinate tetrahedral complex $CoCl_4^{2-}$. There are some important differences regarding principally the energy of the band maxima as shown in Figure 1. The higher energy of these bands as compared with those of $CoCl_4^{2-}$ suggests a stronger average ligand field. The observed shift in the dd absorption can result from substitution of a halo ligand by a nitrogen ligand.

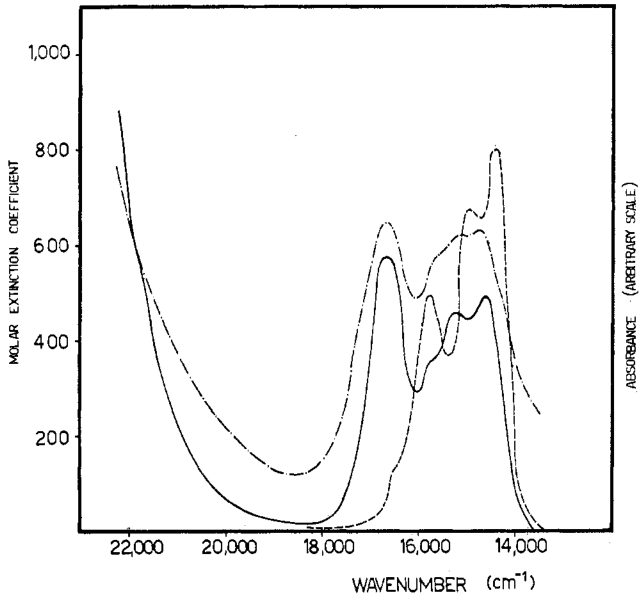

Figure 1.—Absorption spectra: ——, $[Co(dpe)_2(CN)_2]CoCl_3$ in CH_2Cl_2; -----, $[CoCl_4]^{2-}$ in CH_2Cl_2. Reflectance spectrum: –·–·–, $[Co(dpe)_2(CN)_2]CoCl_3$.

By addition of tetraphenylarsonium chloride to dichloromethane solutions of the complex the spectrum gradually changes. The spectra of solutions containing large amounts of Cl^- are identical with those of the $CoCl_4^{2-}$ anion in the same solvent. A spectrophotometric determination of cobalt(II) present as $CoCl_4^{2-}$ carried out at high chloride to cobalt ratios (about 100:1) showed that 1 mol of $CoCl_4^{2-}$ is formed from 1 mol of $Co_2(dpe)_2(CN)_2Cl_3$.

A formulation of the complex as $Co(L^+)Cl_3$, where L^+ is the species $[Co^{III}(dpe)_2(CN)_2]^+$, accounts for the spectral patterns and chemical behavior. The cobalt(II) atom of the $CoCl_3^-$ moiety attains four-coordination by bonding to the nitrogen end of one CN group.[15]

The infrared spectra of the complex in Nujol mull and dichloromethane solution show two bands in the cyanide stretching region and support this formulation. The first absorption at 2108 cm^{-1} falls in the region of the stretching of the terminal CN groups bound to cobalt(III) complexes, near the value of 2113 cm^{-1} observed for the complex $[Co(dpe)_2(CN)_2]ClO_4$. The second absorption at 2146 cm^{-1} can be assigned to the bridging cyanide group according to the observation that bridging cyanide absorbs at higher wave numbers.[16]

Infrared spectra of the complex carried out in CH_2Cl_2 solutions containing excess Cl^- ions show only one absorption at 2113 cm^{-1} which is characteristic for the cation $[Co(dpe)_2(CN)_2]^+$. A bridge-splitting action of the added excess Cl^- is also suggested by visible spectra which show that under these conditions the Co(II) present in the complex is transformed to $CoCl_4^{2-}$.

The dissolution of the complex in donor solvents such as methanol also probably occurs with bridge splitting and formation of L^+ and solvated cobalt(II) species. This is also suggested by the color changes which accompany the dissolution of the complex.

Some solvation is still present in dichloromethane as showed by the slight electrical conductivity (Table II).

$Co(dpe)_2(CN)_2CoX_3$ Complexes.—The complex $Co(dpe)_2(CN)_2CoCl_3$ can also be obtained by addition of $CoCl_2$ to a solution of $[Co(dpe)_2(CN)_2]^+$ in methanol containing an excess of Cl^- ions. Analyses and the spectral pattern show the identity of this complex with the compound prepared *via* oxidation in $C_2H_4Cl_2$ solution.

The same synthetic procedure gave complexes of the type $Co(dpe)_2(CN)_2CoX_3$ (X = Br, NCS). For these complexes the structure $Co(L^+)X_3$ is also suggested on the basis of magnetic moments and infrared spectra (Tables I and III).

The dd electronic spectra display the characteristic features of tetrahedrally surrounded cobalt(II) complexes. The position of the bands is consistent with the spectrochemical series Br < Cl < NCS (Table II).

$Co(dpe)_2(CN)_2MCl_3$ Complexes (M = Mn(II), Fe(II), Ni(II), Zn(II)).—The binding ability of the cation $[Co(dpe)_2(CN)_2]^+$ is also demonstrated by the preparation of a series of complexes with some divalent ions of the first-row transition elements. All of the complexes have the stoichiometry $M(L^+)Cl_3$ where $L^+ = [Co(dpe)_2(CN)_2]^+$ and M = Mn(II), Fe(II), Ni(II), or Zn(II). As the compounds are insoluble or dissolve with solvation in most organic solvents, their investigation was essentially limited to solid-state properties. The X-ray powder diffraction patterns show that all the compounds $M(L^+)Cl_3$ are isomorphous with $Co(L^+)Cl_3$. Hence the structures of these compounds

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can be considered to be virtually identical and consisting of nonionic entities $M(L^+)Cl_3$ where L^+ is the six-coordinate cobalt(III) complex which acts as a positively charged ligand. The divalent metal ion is tetrahedrally surrounded by three chlorine ions and the fourth coordination position is occupied by the nitrogen atom of a bridging cyanide. The pseudotetrahedral coordination of the M(II) ions is supported by the values of the magnetic moments which indicate a high-spin configuration (except for Zn(II)) and are in the range generally found for tetrahedrally coordinated divalent ions (Table I).[10]

The electronic spectra of the $Ni(L^+)Cl_3$ complex also support this formulation showing a broad absorption in the 14,000–17,000-cm^{-1} region which is in agreement with a pseudotetrahedral coordination.[17] Moreover the infrared spectra of all the complexes show two sharp bands in the CN stretching region confirming thus the presence of bridging and terminal cyanide groups. It is pertinent to note that the positive shift observed (19–39 cm^{-1}) is in the range found when organonitriles coordinate through the lone pair of electrons on nitrogen.[18] The small decrease in the ν(CN) for terminal cyanide is in agreement with the observation than when benzodinitriles coordinate to a metal atom through only one cyanide group, the frequency of the remote cyanide is lowered very slightly.[19]

Conclusions

A significant result of this study is the preparation of a novel series of compounds of uncommon stoichiometry and geometry, containing a cobalt(III) complex which acts as a positively charged ligand. The presence of a positive charge which can neutralize by electron delocalization the negative charge of MX_3^- groups probably favors the formation of the compounds $M(L^+)X_3$. The well-known tendency of cyanide to bridge metal atoms[15] affords a viable path to maintain tetracoordination around the divalent ion.

These complexes which may be considered as examples of inorganic zwitterions extend the relatively small number of complexes known to contain a positively charged ligand. In the previously reported $M(L^+)X_3$ complexes L^+ was a cationic phosphorus or nitrogen or arsenic ligand.[20] In the present case L^+ is a transition metal complex containing cyanide groups which behave as an organonitrile coordinated *via* σ bonding to divalent metal ions.

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Mixed-Ligand Complexes of Cobalt(III). Complexes with Stereospecific Tetramine Ligands

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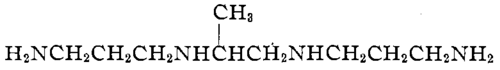
The syntheses, resolution, and properties of some oxalato, malonato, and diacido complexes of cobalt(III) with the stereospecific flexible tetramine ligands 5-methyl-4,7-diaza-1,10-decanediamine (5-Me-3,2,3-tet) and *N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane (picpn) are reported. Stereospecificity is demonstrated by comparison of the optical rotation of the ligand prepared *via* an asymmetric synthesis with that of the ligand isolated from the resolved complex. The stereochemistry of the complexes is deduced from electronic spectra, ORD, and CD measurements.

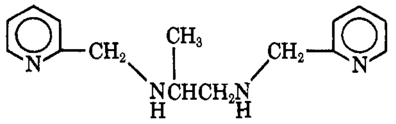
Introduction

To illustrate stereospecific coordination and absolute configuration of some tetramine ligands with cobalt(III), the tetramines 5-methyl-4,7-diaza-1,10-decandiamine, 5-Me-3,2,3-tet (I), and *N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane, picpn (II), were chosen for study. The unique properties of these tetramines lie in the fact that they are not only derivatives of 3,2,3-tet and 2,2,2-tet, respectively, but also contain an optically active center in the ligand affording a means for preparing optically active ligand cobalt(III) complexes. Direct evidence for stereospecific coordination is obtained from a comparison of the cobalt(III) complexes



$$H_2NCH_2CH_2CH_2NH\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2NHCH_2CH_2CH_2NH_2$$

5-methyl-4,7-diaza-1,10-decanediamine
(5-Me-3,2,3-tet)
I



N,N'-bis(2-picolyl)-1-methyl-1,2-diaminoethane
(picpn)
II

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[1] From the M.S. Thesis of J. C., Jr., Illinois Institute of Technology, 1971.