Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, U.S.A.

Five-Coordinate Cobalt(II), Four- and Five-Coordinate Nickel(II), and Six-Coordinate Cobalt(III) Complexes of the Flexible Diphosphine Ligand 1,3-bis(dimethylphosphino)propane[1,2]

John C. Cloyd, Jr.[3] and Devon W. Meek*

Received January 7, 1972

The flexible, aliphatic, diphosphine ligand $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$, dmp, forms the five-coordinate complexes $[M(dmp)_2X]^+$ ($M = Ni$, $X = Cl, Br, I, NCS$; $M = Co$, $X = Cl, Br, I$), as well as the four-coordinate, planar $Ni(dmp)X_2$ and six-coordinate trans*–$[Co(dmp)_2X_2]^+$ complexes. In the case of nickel cyanide, the only isolatable five-coordinate compound corresponded to the dinuclear $Ni_2(dmp)_3(CN)_4$, which contains a bridging diphosphine ligand. All of the complexes were characterized by elemental analyses and by conductance, magnetism, infrared, and electronic spectral measurements. In the five-coordinate nickel series $[Ni(dmp)_2X]^+$, the bromide and iodide complexes appear to possess trigonal-bipyramidal structures, whereas the analogous chloride and thiocyanate complexes have distorted structures of approximately C_s microsymmetry.*

Introduction

A large number of five-coordinate nickel(II) complexes have been characterized during the past seven years, especially with "tripod-like" tetradentate ligands[4-7] and with bidentate ligands containing the *o*-phenylene connecting linkage.[8-10] A much smaller number of pentacoordinate nickel(II) complexes have been isolated with phosphine ligands containing flexible, aliphatic linkages. Several attempts to prepare five-coordinate nickel(II) complexes of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, dpe, have generally been unsuccessful.[11-14] Positive results have been obtained with the diphosphines $RHPCH_2CH_2PHR$ ($R = C_6H_5, C_2H_5$)[15] and $(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$[9] and with the mixed phosphine-thioether ligand $(C_2H_5)_2PCH_2CH_2SC_2H_5$.[16] In all of these three cases, the ligands contain the $–CH_2CH_2–$ linkage between the donor atoms and the resultant complexes have been assigned square-pyramidal complexes on the basis of electronic spectra and an X-ray structural determination[17] of $[Ni(TEP)_2I]I$ (TEP = 1,2-bis(diethylphosphino)ethane, $(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$). Since all of the flexible, tripod ligands $D[CH_2CH_2CH_2As(CH_3)_2]_3$ ($D = P, As, Sb$)[6] and $P(CH_3)_3$ give trigonal-bipyramidal nickel(II) complexes, we considered it probable that the short chelate bite of the *o*-phenylene and the $–CH_2CH_2–$ connecting groups favored formation of the square-pyramidal complexes. In order to test this hypothesis, we prepared the aliphatic diphosphine ligand $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$, which contains a trimethylene connecting linkage and small substituents on phosphorus. Since this diphosphine ligand should exert minimal steric and symmetry effects in the resulting complexes, the coordination geometry of the five-coordinate complexes should reflect the stereochemistry preferred by the metal under the electronic effects of a P_4X set of donor atoms.

This paper reports the preparation and spectral and magnetic studies on some nickel(II), cobalt(II), and cobalt(III) complexes of $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$.

Experimental Section

All synthetic procedures and manipulations of the complexes were performed under a dry nitrogen atmosphere.

---

(1) Presented in the "Symposium of Five-coordinate Complexes" at the 162nd Am. Chem. Soc. National Meeting, Washington, D.C. September 1971, Abstracts no. INORG-96.

(2)This paper is based on part of the Ph.D. dissertation of J. C. Cloyd, Jr. presented to the Graduate School of the Ohio State University in September 1970.

(3)Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research *via* a Graduate Fellowship (No. 781) to J. C. Cloyd, Jr.

(4) L. M. Venanzi, *Agnew. Chem. Intern. Ed. Engl.*, 3, 453 (1964).

(5) G. Dyer and D. W. Meek, *Inorg. Chem.*, 6, 149 (1967), and references contained therein.

(6) G. S. Benner and D. W. Meek, *ibid.*, *6*, 1399 (1967); C. A. Mc Auliffe and D. W. Meek, *Inorg. Chim. Acta.* 5, 270 (1971); E. C. Alyea and D. W. Meek, *J. Am. Chem. Soc.*, *91*, 5761 (1969).

(7) L. Sacconi, *J. Chem. Soc.*, *A*, 248 (1970).

(8) M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, 6, 1543 (1967).

(9) E. C. Alyea and D. W. Meek, *Inorg. Chem.*, *11*, 1092 (1972), and references contained therein.

(10) J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, *92*, 7306 (1970).

(11) C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, *8*, 904 (1969).

(12) M. J. Hudson, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc.*, *A*, 40 (1968).

(13) G. R. Van Hecke and W. DeW. Horrocks, Jr., *Inorg. Chem.*, 5, 1968 (1966).

(14) The five-coordinate complexes $[Ni(R_2PCH_2CH_2PR_2)X]^+$($X = Br, I$, $R = CH_3$; $X = I$, $R = C_2H_5$; $X = I, Br$, $R = C_6H_5$ probably exist in nitrobenzene; however, Booth and Chatt formulated the parent complexes, $Ni(R_2PCH_2CH_2PR_2)_2X_2$ as being six-coordinate in the solid state *cf.*, G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).

(15) K. Issleib and H. Weichmann, *J. Anorg. Allgem. Chem.*, *362*, 33 (1968).

(16) J. F. Sieckhaus and T. Layoff, *Inorg Chem.*, 6, 2185 (1967).

(17) D. F. Rendle and G. J. Palenik, personal communication (1970).

Reagents. Tetramethyldiphosphine disulfide (Orgmet, Inc.), tributylphosphine (Carlisle Chemical Works, Inc.), and 1,3-dichloropropane (Eastman Organic Chemicals) were used without further purification. Treatment of $NiCO_3$ with HBF_4 gave $[Ni(H_2O)_6](BF_4)_2$, which was recrystallized from ethanol. Similarly, $NiCO_3$ and HI gave $[Ni(H_2O)_6]I_2$. All other solvents and reagents were of the finest grade obtainable commercially.

Preparation of 1,3-Bis(dimethylphosphino)propane, (dmp). Both sulfur atoms of tetramethyldiphosphine disulfide were removed by hot tributylphosphine to give tetramethyldiphosphine (73%), b.p. 61-63°/55 torr.[18] Addition of the tetramethyldiphosphine to two equivalents of sodium in liquid ammonia gave $(CH_3)_2PNa$; the red color of this solution was slowly discharged as 1,3-dichloropropane (½ mole ratio) was added dropwise. The bis-phosphine $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$ was isolated as a colorless, foul-smelling liquid, b.p. 62-3°/4 torr (80%).

Treatment of the bis-phosphine with two equivalents of sulfur in benzene produced the disulfide of the ligand in essentially quantitative yield. The latter was recrystallized from dichloromethane, m.p. 226-227.5°.

Anal. Calcd for $C_7H_{18}P_2S_2$: C, 36.83; H, 7.95; S, 28.09. Found: C, 36.25; H, 8.01; S, 28.74.

Preparation of the Four-Coordinate Complexes Ni(dmp)X₂; X = I, Br, Cl, NCS. The appropriate $Ni(H_2O)_6X_2$ salt dissolved in ethanol was added dropwise to a solution of dmp in butanol. The thiocyanate complex precipitated from the reaction solution as soon as the molar ratio Ni/dmp reached 1/1. The halide complexes precipitated as the reaction solutions were concentrated on a hotplate under a stream of nitrogen gas.

Preparation of [Ni(dmp)₂](ClO₄)₂. This complex precipitated immediately as an ethanol solution of $Ni(H_2O)_6(ClO_4)_2$ was added dropwise to dmp in cold butanol.

Preparation of the Five-Coordinate Complexes of [Ni(dmp)₂X]Y; X = I, Br, Y = BF₄; X = NCS, Y = PF₆; X = Cl, Y = B(C₆H₅)₄. In general, an ethanolic solution of "$Ni(H_2O)_6XY$" was prepared and added dropwise to two equivalents of dmp in warm butanol.

For the iodide and bromide complexes, "$Ni(H_2O)_6XY$" was prepared from equimolar amounts of $Ni(H_2O)_6X_2$ and $Ni(H_2O)_6(BF_4)_2$. The iodide complex precipitated immediately from the reaction solution as purple microcrystals. Concertration of the bromide reaction solution gave large red platelets which were slightly impure as indicated by elemental analyses. These crystals were recrystallized from warm butanol.

The chloride and isothiocyanate complexes prepared as above with the tetrafluoroborate counter-ion were impure as indicated by their elemental analyses.

The chloride complex decomposed on attempted recrystallization from ethanol; intractable solids were obtained instead of the original purple microcrystals. The cation, $[Ni(dmp)_2Cl]^+$ however, was isolated by adding an ethanol solution of sodium tetraphenylborate to an ethanol solution of "$Ni(dmp)_2Cl_2$". The purple powder that separated immediately was collected on a frit and briefly air dried. This solid was dissolved in dichloromethane and the solution was filtered to remove the precipitated NaCl. When ethanol was added slowly to the filtrate, large, purple needles crystallized within five minutes. These crystals were collected on a frit and briefly air dried. Within 30 minutes, the needles had changed color from deep purple to deep green in the solid state. These green needles dissolved in dichloromethane to give a purple solution, from which purple needles can again be isolated. The color changes in solution and in the solid state are repeatable several times without apparent decomposition.

The original deeply colored microcrystals of the thiocyanate complex yielded small red rhombohedrons upon recrystallization from ethanol. Elemental analyses for these crystals indicated the formulation $Ni_2(dmp)_3(NCS)_2(BF_4)_2$. When an ethanol solution containing equimolar amounts of $Ni(NCS)_2$ and $NaPF_6$ was added to dmp in cold butanol, the complex, $[Ni(dmp)_2NCS]PF_6$ precipitated immediately as deep green microcrystals.

Preparation of Ni(dmp)(CN)₂ and Ni(dmp)₁.₅(CN)₂. Equimolar amounts of dmp and anhydrous $Ni(CN)_2$ were combined in hot butaenol. The $Ni(CN)_2$ dissolves rapidly to give a red solution. After briefly stiring this solution, the solvent was removed *in vacuo* and the red residue was dissolved in dichloromethane. The resulting solution was filtered and an equal volumn of petroleum ether (b.p. 30° –60°) was added. On concentration of this solution under a gentle stream of nitrogen. blocky, yellow crystals separated. Further concentration of the filtrate led to deposition of a red oil. Consequently, the yellow crystals, which subsequently proved to be $Ni(dmp)(CN)_2$, were collected and the solvent was removed from the red filtrate *in vacuo*. The resulting red solid was dissolved in equal volumes of dichloromethane and di-isopropyl ether. Slow concentration of this solution under nitrogen initially gave a small amount of a mixture of the yellow crystals and some red crystals; this mixture was removed by filtration. When most of the dichloromethane had evaporated from the remaining filtrate, red crystals began to separate. The flask was stoppered and cooled; a large quantity of the red crystals of $Ni(dmp)_{1.5}(CN)_2$ were obtained.

Preparation of [Co(dmp)₂X]B(C₆H₅)₄, X = Cl, Br; and Co(dmp)₂I₂. A deep green solution developed immediately when anhydrous CoX_2 (X = Br or Cl) was added to an ethanol solution containing two equivalents of dmp. Addition of an ethanol solution of sodium tetraphenylborate to the above solution produced deep green microcrystals immediately. These crystals were collected and recrystallized from dichloromethane-ethanol.

An ethanol solution of "$Co(H_2O)_6I_2$" was prepared

---

[18] G. W. Parshall, *J. Inorg. Nucl. Chem.*, *14*, 291 (1960); L. Maier, *ibid.*, *24*, 275 (1962).

in situ from $Co(H_2O)_6(NO_3)_2$ and NaI and added dropwise to two equivalents of dmp in warm ethanol. A deep green solution was formed immediately and after two minutes, a large amount of deep green crystals had precipitated. These were collected on a sintered-glass frit and briefly air dried.

Preparation of $[Co(dmp)_2X_2]ClO_4$ *X = Cl, Br, I.* Two equivalents of dmp were mixed with one equivalent of CoX_2 (X = Br or Cl) or $Co(H_2O)_6I_2$ (see above), and one equivalent of $NaClO_4$ in ethanol. The resulting solution was stirred rapidly as one drop of aqueous, concentrated HX was added; air was then bubbled through the solution for six hours. Solvent was added periodically to maintain the volume of the solution between 50 and 70 ml. The volume of the solution was finally reduced to ~20 ml and the solid, which had separated, was collected on a funnel. This precipitate was dissolved in a minimum amount of warm dimethylformamide, and ethanol (50-70 ml) was added. The solutions were kept at $-10°$ for two days, during which green (Br, Cl) or violet (I) platelets separated.

Spectral, Conductance, and Magnetic Measurements. These measurements were obtained as described previously.[19] Solid state electronic spectra at 77°K were obtained as Nujol mulls of the sample immersed in liquid nitrogen in a quartz dewar.

Results and Discussion

Four-Coordinate Nickel(II) Complexes. With the exception of the cyanide complexes, which were prepared by adding solid, anhydrous $Ni(CN)_2$ to the ligand 1,3-bis(dimethylphosphino)propane, dmp, in hot *n*-butanol, the nickel complexes were prepared by adding an ethanol solution of the appropriate Ni^{II} salt to *n*-butanol solutions of dmp under a dry nitrogen atmosphere. In the cases of the $Ni(dmp)X_2$ complexes, X = halide or NCS, initial addition of the Ni^{II} solution to the ligand solution probably results in the formation of a five-coordinate nickel(II) complex, *e.g.*, $[Ni(dmp)_2X]^+$. This supposition was indicated by immediate formation of an intensely colored solution which subsequently changed to the color of the appropriate $Ni(dmp)X_2$ compound as the ratio Ni:dmp approached 1:1 during the addition of the NiX_2 solution. The $Ni(dmp)X_2$ complexes are diamagnetic (Table I) and are stable indefinitely in the solid state; however, the compounds decompose in solution within a few hours.

The infrared spectra of the cyanide and the thiocyanate complexes, both in solution and in the solid state, show two sharp peaks in the C$\equiv$N stretching region; in acetonitrile the two peaks of the thiocyanate complex occur at 2092 and 2111 cm^{-1}. The integrated absorption intensities of these bands are $11.0 \times 10^{-4} M^{-1} cm^{-1}$ and $9.08 \times 10^{-4} M^{-1} cm^{-1}$, respectively; both values are indicative of N-bonded thiocyanate groups.[20] In dichloromethane the cyanide compound has two sharp infrared peaks at 2112 and 2124 cm^{-1}. These data are consistent with a *cis* planar structure. The visible electronic spectra, with a single d–d transition at 24,400 and 30,100 cm^{-1} for the isothiocyanate and cyanide complexes, respec-

Table I. Characterization and Analytical Data for the 1,3-bis(dimethylphosphino)propane Complexes.

Compound	Color	$10^6\chi_M$ [a]	Λ_M [b]	C Calcd.	C Found	H Calcd.	H Found	Hal Calcd.	Hal Found
$[Ni(dmp)_2NCS]PF_6$ [c]	Green	302	146	30.54	30.83	6.15	6.25	2.37	2.31 [g]
$[Ni(dmp)_2Cl]B(C_6H_5)_4$	Green	243	106	61.53	61.49	7.61	7.87	4.78	5.03
$[Ni(dmp)_2Br]BF_4$	Red	130	150	30.36	30.42	6.55	6.71	14.43	14.48
$[Ni(dmp)_2I]BF_4$	Purple	177	150	27.99	27.19	6.02	6.01	21.12	21.37
$Ni(dmp)_{1.5}(CN)_2$	Red	65	0.08	42.04	41.35	7.62	7.77	7.85	7.67 [g]
$Ni(dmp)(CN)_2$	Yellow	81	1.00	39.32	39.32	6.60	6.32	10.19	10.02 [g]
$Ni(dmp)(NCS)_2$	Yellow	137	2.51	31.89	31.81	5.35	5.37	8.27	8.16 [g]
$Ni(dmp)Cl_2$	Yellow	95	0.028 [d]	28.62	28.55	6.17	6.18	24.14	24.38
$Ni(dmp)Br_2$	Red	108	0.224 [d]	21.97	21.86	4.74	4.69	41.76	41.80
$Ni(dmp)I_2$	Purple	490	— [e]	17.64	17.70	3.81	3.69	53.24	53.44
$[Ni(dmp)_2](ClO_4)_2$	Yellow	600	195 [f]	28.71	28.00	6.19	6.06	12.10	11.94
$[Co(dmp)_2Cl]B(C_6H_5)_4$	Green	1475	110	61.51	61.44	7.61	7.66	4.78	5.04
$[Co(dmp)_2Br]B(C_6H_5)_4$	Green	1509	110	58.04	58.17	7.18	7.23	10.16	10.41
$[Co(dmp)_2I]I$	Green	1650	147	26.24	26.20	5.66	5.72	39.59	39.37
$[Co(dmp)_2Cl_2]ClO_4$	Green	140	99.3 [h]	30.16	30.08	6.51	6.57	19.08	18.88
$[Co(dmp)_2Br_2]ClO_4$	Green	147	97.6 [h]	26.02	26.15	5.61	5.87		
$[Co(dmp)_2I_2]ClO_4$	Violet	145	90.3 [h]	22.71	22.45	4.90	5.12		

[a] χ_M is the corrected molar susceptibility of the compound in cgs units. The μ_{eff} values calculated from these data for the cobalt(II) complexes at 25° are 1.88±0.01 B.M. (Cl) and 1.91±0.01 (Br), and 1.98±0.01 B.M. (I). [b] Molar conductance values obtained on freshly prepared $\sim 10^{-3}$ solutions in acetonitrile. Uni-univalent perchlorate and tetrafluoroborate salts of large cations usually give values of 140-160 in acetonitrile. Tetraphenylborate salts exhibit markedly lower Λ_M values, owing to the lower specific conductance of this large anion. [c] The abbreviation, dmp, is for the ligand, 1,3-bis-(dimethylphosphino)propane $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$, of the compound. [d] Measured in freshly prepared 1,2-dichloroethane solutions. The molar conductance of $\sim 10^{-3} M$ solution of tetra-n-butylammonium iodide in this solvent is 23.3 cm^2/ohm mol. [e] No reliable value obtained. Freshly prepared solutions dissociate before measurements can be taken. [f] Conductance value of $\sim 10^{-3} M$ solution in nitromethane. Divalent-univalent electrolytes exhibit molar conductance values of ~150-190 cm^2/(ohm mol) in this solvent [g] Nitrogen analysis. [h] Approximately $10^{-3} M$ nitromethane solution.

(19) T. D. DuBois and D. W. Meek, *Inorg. Chem.*, *6*, 1395 (1967).

(20 D. W. Meek, P. E. Nicpon, and V.I. Meek, *J. Am. Chem. Soc.*, *92*, 5351 (1970).

tively, also support a four-coordinate, planar geometry in both the solid state and in solution.

The corresponding diphenylphosphino ligand, 1,3-bis(diphenylphosphino)propane (dmp), also forms Ni-LX_2 complexes.[13] The latter complexes are diamagnetic in the solid state; however, in solution the nickel halide-dpp complexes exhibit increasing paramagnetism in the order I > Br > Cl. The $Ni(dmp)X_2$ complexes (X = Br and Cl), on the other hand, do not exhibit any paramagnetic behaviour. This result would be expected on the basis of the increased ligand field strength of the dimethylphosphino donors as compared to the diphenylphosphino groups.

Five-Coordinate Nickel(II) Complexes. Physical data for the $[Ni(dmp)_2X]^+$ complexes are listed in Table I. The conductivity values for the tetrafluroborate and hexafluorophosphate salts fall within the range for uni-univalent electrolytes in acetonitrile; the lower value for the tetraphenylborate salt can be attributed to the lower specific conductance observed for the large tetraphenylborate anion.[21]

Isolation of the pentacoordinate cations $[Ni(dmp)_2X]^+$ (X = halide, NCS) is facilitated by using large poorly-coordinating anions such as BF_4^-, PF_6^-, and $B(C_6H_5)_4^-$. In the presence of the large ions, crystallization of the complexes $[Ni(dmp)_2X][anion]$ from non-aqueous solutions takes place rapidly and before significant decomposition of the five-coordinate cations occurs.

The geometries of these five-coordinate $[Ni(dmp)_2X]^+$ cations, as deduced from electronic spectra, occur in two distinct forms. Note in Figure 1 that the electronic spectra of the iodide and bromide complexes in the region 16,000-22,000 cm^{-1} resemble each other closely, but that they differ significantly from the spectra of the chloride and thiocyanate. (The latter two complexes have similar spectral profiles.) The spectra of the iodide and bromide complexes, both in solution and in the solid state, (Figure 2) compare favorably with those of known trigonal-bipyramidal diamagnetic nickel(II) complexes.[4-6] The spectra of the cations $[Ni(dmp)_2X]^+$ (X = NCS and Cl), on the other hand, have two strong absorptions in the 14,000-24,000 cm^{-1} region and most closely resemble those of nickel(II) complexes that are known to have distorted square pyramidal structures.[9,22] The spectral similarity is illustrated in Figure 3; note also that the maxima for the $[Ni(dmp)_2Cl]B(C_6H_5)_4$ complex are shifted to lower energy as compared to those of $[Ni(TEP)_2I]B(C_6H_5)_4$ (TEP = $(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$). The spectral shift results from the lower ligand field strength of the six-member chelate ring as compared to the five-member ring.

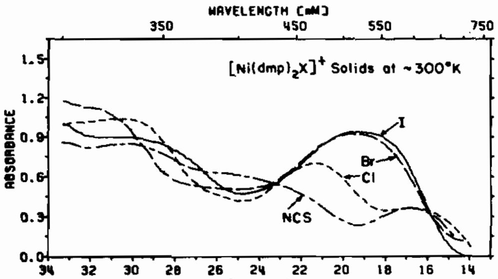

Figure 1. Electronic spectra of the $[Ni(dmp)_2X]^+$ solid complexes suspended in Nujol at ~300°K: I,——; Br,— — —; Cl,- - - - -; NCS — - — - —.

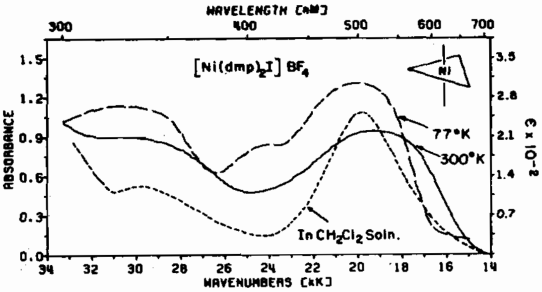

Figure 2. Electronic spectra of $[Ni(dmp)_2I]BF_4$ as a solid in Nujol at 300°K ——— and at 77°K — — — and in a dichloromethane solution at ~300°K - - - - -.

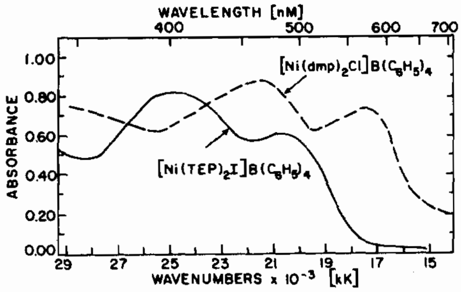

Figure 3. Electronic spectra of the solid five-coordinate $[Ni(TEP)_2I]B(C_6H_5)_4$ ——— and $[Ni(dmp)_2Cl]B(C_6H_5)_4$ - - - - - complexes suspended in Nujol at 77°K. The absorbance scale is arbitrary.

The geometry of the inner coordination sphere of the distorted $[Ni(bidentate)_2X]^+$ complexes would have C_s microsymmetry. As a twisting distortion from either idealized five-coordinate structure (*i.e.* a trigonal bipyramid or a square pyramid) would produce a C_s microsymmetry, it is a moot point to label the structures of the chloride and thiocyanate complexes as being either a distorted trigonal bipyramid or a distorted square pyramid. In any case, the electronic spectra fit an intermediate structure of C_s microsymmetry better than a coordination geometry approximating either C_{4v} or D_{3h} microsymmetry.

A red crystalline complex is isolated when equimolar amounts of anhydrous $Ni(CN)_2$ and dmp are mixed in *n*-butanol, in addition to the yellow planar

---

(21) G. J. Janz, F. J. Kelly, and H. V. Venkatasetty, "A Survey of Non-Aqueous Conductance Data", Rensselaer Polytechnic Institute, Troy, N. Y., 1962.

(22) J. C. Cloyd, Jr. and D. W. Meek, submitted for publication; G. J. Palenik, personal communication[23] concerning the structures of $[Ni(TEP)_2I]I$ and $[Ni(dap)(CN)_2]$ (TEP=$(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$ and dap=$C_6H_5P[CH_2CH_2CH_2As(CH_3)_2]_2$. Both complexes have somewhat distorted square pyramidal structures of C_s symmetry and give electronic absorption bands in the visible region very similar to those shown in Figure 1 for the thiocynate and chloride complexes of $(CH_3)_2PCH_2CH_2CH_2P(CH_3)_2$. For example, note the contours in the spectrum of $[Ni(dap)(CN)_2]$ given in Figure 4.

compound Ni(dmp)$(CN)_2$. The elemental analyses indicate 1.5 diphosphine ligands per nickel dicyanide (Table I). The complex is a non-conductor in acetonitrile, and a molecular weight measurement in benzene gave a value of 805 (theory for the dimer = 714). The complex is diamagnetic and its electronic spectrum (illustrated in Figure 4) is very similar to that of Ni(dap)$(CN)_2$, were dap = $C_6H_5P[CH_2CH_2CH_2As(CH_3)_2]_2$. The latter complex has a square-pyramidal structure, proven by a X-ray structure determination, with one cyanide in the basal plane and one apical cyanide.[22] Thus, the electronic spectrum of $Ni_2(dmp)_3(CN)_4$ strongly indicates a five-coordinate structure approximating a square pyramid.

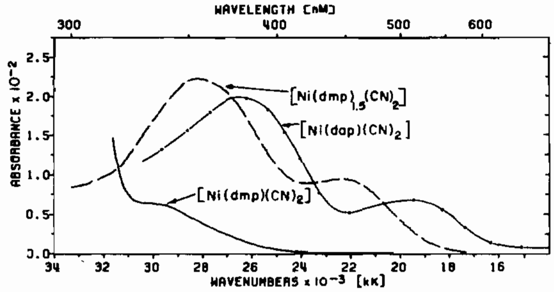

Figure 4. Electronic spectra of Ni(dmp)$(CN)_2$ ——— and Ni$(dmp)_{1.5}(CN)_2$ — — — — in dichloromethane solution and of solid Ni(dap)$(CN)_2$ at 77°K —·—·—·—.

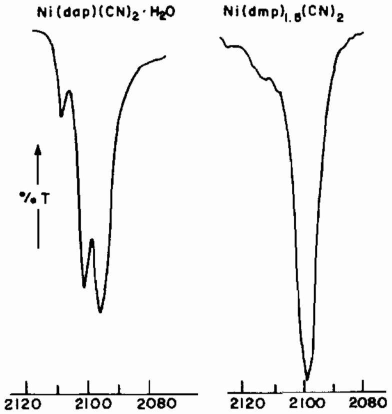

Figure 5. C≡N stretching region of the infrared spectra of the Ni(dap)$(CN)_2 \cdot H_2O$ and Ni$(dmp)_{1.5}(CN)_2$ complexes in dichloromethane.

The infrared spectrum of $Ni_2(dmp)_3(CN)_4$ is useful in determining which of the ligand groups forms a bridge between the two nickel atoms. The spectrum (Nujol mull) exhibits a sharp, intense band at 2090 cm^{-1} and a weak spike at 2100 cm^{-1}. In the dichloromethane solution, these absorptions occur at 2100 cm^{-1} and 2115 cm^{-1} respectively. Figure 5 shows that the C≡N stretching region of Ni(dap)$(CN)_2$ and $Ni_2(dmp)_3(CN)_4$ differ significantly. Thus, the infrared spectrum tends to exclude a square-pyramidal structure similar to that of Ni(dap)$(CN)_2$, where both cyanides are terminal and where the apical cyanide has a significantly longer Ni–C bond distance (2.188 (11) Å *vs.* 1.860 (11) Å) than does the cyanide in the basal plane.[23] Also, a bridging cyanide can be excluded on the basis that its C≡N stretching frequency should be shifted ~30-40 cm^{-1} to higher values.[24] Since the electronic spectra indicate a square-pyramid and the infrared spectra indicate the absence of both apical and bridging cyanides, we propose that one of the diphosphine ligands functions as the bridge. The square-pyramidal structure represented in Figure 6, and proposed tentatively, would have approximately C_s microsymmetry and would be consistent with the experimental electronic and infrared spectra, if one assumes that the nickel atom is close to the basal plane of the $P_2(CN)_2$ set of donor atoms. If this is true, the symmetric stretch of the Ni$(CN)_2$ unit would be weak, consistent with the the observed spectrum. The same type of structure, as represented in Figure 6, has been proposed for Ni$(dpp)_{1.5}(CN)_2$ and Co$(dpp)_{1.5}(CN)_2$, where dpp = bis(diphenylphosphino)-propane.[25]

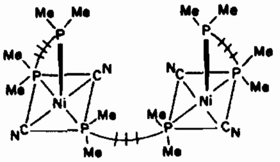

Figure 6. A proposed structure for the dimeric Ni$(dmp)_{1.5}(CN)_2$ compound.

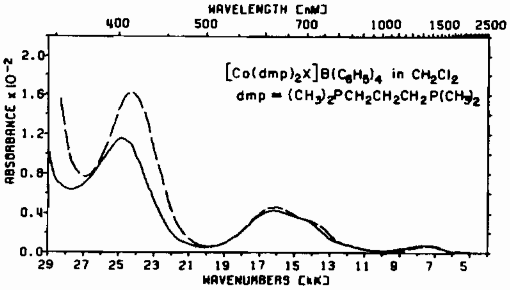

Figure 7. Electronic spectra of the $[Co(dmp)_2X](BC_6H_5)_4$ complexes in dichloromethane: X=Cl (———), X—Br (— — —).

Five-Coordinate Cobalt(II) Complexes. When two equivalents of the ligand dmp and one equivalent of CoX_2 are mixed in ethanol under dry nitrogen, the solution becomes dark green immediately. In the case of the iodide, dark green crystals of $[Co(dmp)_2I]I$ precipitate from a concentrated solution. The corresponding dichloride and dibromide complexes are more soluble; thus the $[Ni(dmp)_2X]^+$ cations (X = Cl, Br) were isolated as the tetraphenylborate salts. On standing a few hours under nitrogen, dichloromethane solutions of the complexes are slowly converted to the Co^{III} complexes as indicated by changes in the electronic spectra of the solutions.

(23) G. J. Palenik, personal communication (1970).

(24) J. Reedijk, A. P. Zuur, and W. L. Groneveld, Rec. Trav. Chim., 86, 1127 (1967), and references cited therein.

(25) P. Rigo, B. Corain, and A. Turco, *Inorg. Chem.*, 7, 1623 (1968); P. Rigo, M. Bressan, and A. Turco, *ibid.*, 7, 1460 (1968).

Table II. Electronic Spectra of Four-coordinate Nickel(II)-dmp Complexes.

Complex	Solution (CH_2Cl_2), cm^{-1} (ε_{max})	Solid State, cm^{-1}	
		~300°K	77°K
Ni(dmp)Cl_2	22,000 (705)	21,900	22,450
	34,500 (5,200)		
	38,000 (16,400)		
	43,500 (17,200)		
Ni(dmp)Br_2	21,050 (720)	20,600	21,270
	27,200 (940)		
	33,000 (5,300)		
	36,000 (10,400)		
	40,800 (19,600)		
Ni(dmp)I_2	—[a]	19,600B[b]	20,000 B[b]
Ni(dmp)$(NCS)_2$	24,400 (1,470)[c]	—[d]	—[d]
	36,350 (14,100)		
	43,600 (32,600)		
Ni(dpm)$(CN)_2$	30,100 S[b] (649)	—[d]	—[d]
	32,900 S[b] (3,330)		
	34,700 (4,100)		
$Ni(dmp)_2(ClO_4)_2$	22,270 (660)[e]	22,100	22,750

[a] Decomposes. [b] B, broad; S, shoulder. [c] Acetonitrile solution. [d] Not measured. [e] Nitromethane solution.

Table III. Electronic Spectra of Pentacoordinate Nickel(II)-dmp Complexes.

Complex	Solution, CH_2Cl_2 cm^{-1} (ε_{max})	Solid State, cm^{-1}	
		~300°K	77°K
$[Ni(dmp)_2I]BF_4$	19,800 (2,510)	19,300	20,000
	29,400 (1,240)	30,800 S[a]	24,100 S[a]
	38,450 (22,000)		30,800
$[Ni(dmp)_2Br]BF_4$	20,400 (1,740)	19,500	20,000
	30,800 (2,650)	32,300 S	25,000
	39,200 (22,200)		32,100
$[Ni(dmp)_2Cl]B(C_6H_5)_4$	16,700 S (610)	16,700	17,500
	20,800 (1,375)	21,400	21,75
	31,400 (6,150)	30,800	27,800 S
	34,500 S (6,600)		30,300
$[Ni(dmp)_2NCS]PF_6$	17,600 (647)	16,800	16,950
	22,450 (1,270)	25,000 S	23,800
	29,800 (3,290)	30,300	27,000
	37,750 (22,400)		30,300
$[Ni(dmp)_{1.5}(CN)_2]_2$	22,350 (949)[b]	—[c]	—[c]
	28,200 (2,230)		

[a] B, broad; S, shoulder. [b] ε_{max} calculated on the basis of the dimeric formula. [c] Not measured.

Table IV. Electronic Spectra of Pentacoordinate Cobalt(II)-dmp Complexes.

	Solution, CH_2Cl_2, cm^{-1} (ε_{max})	Solid State, cm^{-1}	
		~300°K	77°K
$[Co(dmp)_2Cl]B(C_6H_5)_4$	7,530 (69)	7,700	7,800
	14,300 S[a] (316)	11,900 S[a]	12,700 S[a]
	16,400 (419)	16,100 B[a]	14,200
	24,800 (1120)	24,800	16,100
	31,800 (7610)	31,000	25,000
$[Co(dmp)_2Br]B(C_6H_5)_4$	7,250 (69)	7,600	7,700
	14,100 S (312)	11,900 S	12,500 S[a]
	16,100 (455)	15,000 B	14,000
	24,300 (1620)	23,900	16,000
	31,200 (6310)	29,850	24,600
$[Co(dmp)_2I]I$	6,400 (42)[b]	6,700	6,700 B
	13,500 S (166)	13,500	13,400
	16,000 (330)	16,400	16,250
	23,800 (1020)	23,700	23,850

[a] B, broad; S, shoulder. [b] In acetonitrile solution.

The conductivity data for the $[Co(dmp)_2X]^+$ complexes (Table I) are consistent with uni-univalent electrolytes,[21] indicating the presence of the pentacoordinate $[Co(dmp)_2X]^+$ cation in solution. The magnetic moments (Table I) indicate one unpaired electron, and are similar to those of other pentacoordinate, low-spin Co^{II} complexes.[26] The electronic spectra are given in Table IV, and are best interpreted in terms of a square pyramidal structure with an apical halide. In fact, the relative positions and intensities of the absorption bands (Figure 7) are remarkably similar to those of the square-pyramidal cation $[Co(diphos)_2Cl]^+$ (diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, whose structure has been determined recently by X-ray crystallography.[27] Thus, the electronic transitions observed for the $[Co(dmp)_2X]^+$ series may be assigned on the basis of a C_{4v} energy level diagram for Co^{II}.[26]

Six-Coordinate Cobalt(III) Complexes. The Co^{III} complexes $[Co(dmp)_2X_2]ClO_4$ (X = Cl, Br, I) are readily prepared by air oxidation of acidic (HX) ethanol solutions of the Co^{II} complexes. The complexes are diamagnetic and uni-univalent electrolytes in nitromethane. Their electronic spectra exhibit two d–d transitions which are assigned to the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions of a *trans*-octahedral complex, *i.e.* D_{4h} microsymmetry. The electronic spectra (Table V) produce the usual spectrochemical series, *i.e.* I < Br < Cl, and the reduction of the Racah parameter B follows the nephelauxetic series.

Table V. Electronic Spectral and Conductance Data on the *trans*-$[Co(dmp)_2X_2]ClO_4$ Complexes.

X	E_{max}, cm^- (ε_{max})	Λ_M cm^2/ohm mole
I	16,700 (154) 26,500 (5560)	99.3
Cl	15,900 (128) 24,100 (2910)	97.6
Br	14,800 (100) 17,600 (4565)	90.3

Acknowledgment. The authors are grateful for the financial support, of the National Science Foundation.

---

(26) G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, *89*, 3963 (1967).
(27) J. Stalick, P. W. Corfield, and D. W. Meek, *ibid.*, *94*, (Aug. 23, 1972).