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Four- and Five-Coordinate Complexes of Ni^{II} with a Four-Atom-Ring Chelating Diphosphine and Their Oxidation Products

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Nickel(II) halides react under controlled conditions with the diphosphine bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$ (dpm), forming the monomeric, four-coordinate, low-spin chelate complexes [NiX_2(dpm)], where X is Cl, Br, or I. The four-coordinate monomer [NiI_2(dpm)] can be transformed into a five-coordinate, low-spin iodo-bridged dimer [Ni_2I_4(dpm)$_2$], which in turn reverts slowly to the monomer when dissolved in dichloromethane. A similar five-coordinate dimer, stable only in the solid state, is formed by dpm with nickel(II) thiocyanate. The complexes [NiX_2(dpm)] are remarkably stable both in the solid state and in solution, although the diphosphine forms a highly strained four-atom chelate ring. Above 220°, however, the coordinated diphosphine slowly undergoes air-oxidation resulting chiefly in the formation of nickel(II) complexes of the related diphosphine, dioxide, $Ph_2P(O)CH_2P(O)Ph_2$ ($dpmO_2$). These oxidation products are identical with the complexes [Ni($dpmO_2$)$_3$][NiX_4] (octahedral tris-chelate cation, tetrahedral anion with X = Cl, Br, or I), obtained directly by reaction of nickel(III) halides with the O-donor chelating $dpmO_2$ ligand.

Introduction

Among the many diphosphine ligands which have been extensively investigated in recent years, bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$ (dpm) has received comparatively little attention,[2a-f] probably because it was thought that the closeness of its two P-donor atoms would sterically hinder the formation of stable chelate rings with metal ions. In fact, the results reported by several investigators[2a,c] indicated that dpm would coordinate to Ni^{II} through only one of its P-donor atoms, forming complexes of the type [NiX_2(dpm)$_2$]. Some bis-chelate complexes of the type [M(dpm)$_2$]X_2 where, however, obtained[2a] with heavier transition metals such as Pd^{II} and Pt^{II}, which have a much stronger affinity for tertiary phosphines.

We first became interested in the Ni^{II} complexes of monodentate dpm during some preliminary investigations of the donor properties of positively charged P-donor ligands.[3] We thought that the [NiX_2(dpm)$_2$] species might readily undergo quaternization at the uncoordinated P-atom, thus providing a convenient route for the syntheses of Ni^{II} complexes of positively charged phosphines. We were somewhat surprised when our repeated attempts to carry out such a quaternization reaction under a wide variety of conditions consistently failed to yield the desired Ni^{II} complexes of the monoquaternized dpm ligand. Instead, we obtained variable amounts of the "free" diquaternized diphosphine cation, together with a mixture of Ni^{II} complexes whose chief components were identified as the new species [NiX_2(dpm)], in which dpm is present as a chelating ligand. Once we realized that the diphosphine $Ph_2PCH_2PPh_2$ can act as a chelating ligand also toward Ni^{II}, we had no difficulty in finding conditions suitable for the direct preparation of the chelate complexes [NiX_2(dpm)] from Ni^{II} halides and the diphosphine. This paper describes the preparation, structural characterization, and the very interesting spontaneous air-oxidation of a series of Ni^{II} complexes containing dpm as a four-atom-ring chelating ligand.

Experimental Section

Phisical Measurements. d-d Electronic spectra, vibrational spectra, magnetic susceptibilities, and X-ray powder diffractographs were obtained as previously described.[3] *Mass spectra* were recorded with an AEI MS 902 model mass spectrometer. *Thermal decomposition studies* were carried out with a Dupont 900 Differential Thermal Analyzer equipped with a 950 Thermogravimetric attachment, using both a dry air and a dry nitrogen purge.

Preparation and Characterization of the Complexes. The halo-complexes of monodentate dpm, [NiX_2(dpm)$_2$], were prepared as previously described,[2e] and had the correct analyses and magnetic properties.

The chelate monomers, [$NiCl_2$(dpm)], [$NiBr_2$(dpm)] and [NiI_2(dpm)], were prepared as follows: A nearly saturated solution of dpm in isobutanol-nitromethane (2:1) at 80° as added dropwise and with stirring

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to a hot saturated solution of the anhydrous Ni^{II} halide in the same solvent mixture. A very dark-colored solution (brown for the chloride and bromide, purple for the iodide) was obtained and upon heating for 10 min at 80° dark colored needle-like crystals began to separate. The mixture was then diluted with about one tenth of its volume of triethylorthoformate, and cooled in a refrigerator for several hr. The dark colored crystalline products were filtered off, washed with cold isobutanol and triethylorthoformate, and dried *in vacuo*. Yields: 75-85%. The complexes thus obtained were well-crystallized and analytically pure. If desired, the chloro- and bromo-complexes could be recrystallized by dissolving them in a 1:1 mixture of dichloromethane-nitromethane, filtering off the small solid residue, and diluting the filtered solution with triethylorthoformate. The iodo-complex could not be recrystallized, for under all the conditions tried it changed in part either to the olive-green dimer $[Ni_2I_4(dpm)_2]$, or to the purple bis-diphosphine complex $[NiI_2(dpm)_2]$.

Analyses. Calcd for $C_{25}H_{22}Cl_2P_2Ni$: C, 58.42; H, 4.32; Cl, 13.79. Found: C, 58.5; H, 4.4; Cl, 13.8%. Calcd for $C_{25}H_{22}Br_2P_2Ni$: C, 49.80; H, 3.68; Ni, 9.74. Found: C, 50.1; H, 3.9; Ni, 9.5%. Calcd for $C_{25}H_{22}I_2P_2Ni$: C, 43.08; H, 3.18; I, 36.42. Found: C, 43.1; H, 3.2; I, 36.1%. The $[NiX_2(dpm)]$ complexes were also obtained by other procedures. For example, $[NiBr_2(dpm)]$ was formed whenever the complex $[NiBr_2(dpm)_2]$ (m.p. 110°) was refluxed in acetone for several hr (yields, 80%), or was treated with an alkyl halide in the attempt to mono-quaternize the mono-dentate dpm ligands (yields, 25%), or was dissolved in dichloromethane and treated with twice the volume of triethylorthoformate (yields, 60%).

Solubility. The complexes $[NiX_2(dpm)]$ are moderately soluble in dichloromethane and acetonitrile; slightly soluble in alcohols, acetone, and nitromethane; insoluble in most other solvents (they dissolve with decomposition in chloroform).

Thermal Behavior and Air-Oxidation. The complexes $[NiX_2(dpm)]$ are stable to air at room temperature and are not affected by moisture. When heated the complexes do not melt; in a dry nitrogen atmosphere they decompose above 250° with a sharp weight loss corresponding to sublimation of the diphosphine ligand (the decomposition temperatures are listed in Table I). In the presence of dry oxygen or air at high temperature the complexes slowly change color while their mass increases slightly; the brown chloro-complex begins to turn light-blue at 220-230°; the red-brown bromo-complex begins to turn green at 225-230°, and the purple iodo-complex begins to turn brik-red at 210-215°. For all three compounds, the color change is complete after prolonged heating at 260-270°. The resulting products were identified, on the basis of their vibrational and *d-d* electronic spectra, as consisting chiefly of the ionic species $[Ni(dpmO_2)_3][NiX_4]$, described later. The mass increase accompanying the color change of $[NiBr_2(dpm)]$ from red-brown to green was consistently found to be 5.2% (Calcd for the uptake of two oxygen atoms per diphosphine ligand, 5.3%). For the chloro- and iodo-complexes, the observed mass increase was less than expected (Calcd for the chloro-complex, 6.2; found, 4.1%. Calcd for the iodo-complex: 4.6; found, 1.7%). However, in these latter experiments the color change was accompanied by sublimation of some diphosphine ligand for the chloro-complex, and of both diphosphine and iodine for the iodo-complex.

The Dimer $[Ni_2I_4(dpm)_2]$. The finely ground purple monomer $[NiI_2(dpm)]$ was suspended in acetone and the mixture was refluxed for 3 hr. The color of the suspended solid gradually changed from purple to dark olive-green, while the solution remained purple. The olive-green powder was filtered, washed with cold acetone, and dried *in vacuo*. Yields, 90%.

Analyses. Calcd for $C_{25}H_{72}I_2P_2Ni$: C, 43.08; H, 3.18; I, 36.42. Found: C, 43.4; H, 3.3; I, 36.6%. The same compound was also obtained, as small shiny black prisms that grind to an olive-green powder, by dissolving the purple $[NiI_2(dpm)]$ in dichloromethane, diluting the resulting purple solution with a small volume of triethylorthoformate, and allowing the solution to evaporate slowly at room temperature (yields, 95%). The compound was also formed in 90% yields when $[NiCl_2(dpm)]$ or $[NiBr_2(dpm)]$ was suspended in acetone containing 20% of CH_3I (as a source of I^-) and refluxed with stirring for 3 hr.

Solubility and Thermal Behavior. The complex $[Ni_2I_4(dpm)_2]$ dissolves very slightly in dichloromethane giving an olive-green solution which slowly changes to purple. In most other solvents the complex is insoluble at first; however, upon prolonged standing in nitromethane, acetonitrile, and hot alcohols it dissolves slightly giving purple solutions identical to those of the monomeric $[NiI_2(dpm)]$. The stability and thermal behavior of the olive-green $[Ni_2I_4(dpm)_2]$ closely resemble those of the purple isomer, $[NiI_2(dpm)]$.

Trans-$[Ni(NCS)_2(dpm)_2]$. A hot saturated solution of the ligand was added dropwise and with stirring to a solution of $Ni(NCS)_2 \cdot 1/2H_2O$ in hot isobutanoyl (Ni-ligand mole ratio, 1:2.5). The reaction mixture was heated at 100° with stirring for one-half hr, and the orange precipitate that formed was filtered off, washed with isobutanol and dried *in vacuo*. The compound thus obtained was beautifully crystalline and analytically pure. It desired, it could be recrystallized by dissolving it in dichloromethane containing some added ligand, filtering off the small solid residue, diluting the filtered solution with triethylorthoformate, and cooling it for several hr at 0°.

Analyses. Calcd for $C_{50}H_{44}P_4(NCS)_2Ni$: Ni, 6.22; NCS^-, 13.31. Found: Ni, 6.4; NCS^-, 12.8%. The complex melts at 168-169° with decomposition. It is readily soluble in dichloromethane, chloroform, and nitromethane, only slightly soluble or insoluble in acetone, alcohols and benzene.

The Dimeric $[Ni_2(NCS)_4(dpm)_2]$ was prepared as follows: A sample of the *trans*-$[Ni(NCS)_2(dpm)_2]$ was dissolved in a minimum amount of dichloromethane and the resulting solution was allowed to stand at room temperature for several hours. The brick-red solid that separated was filtered off, washed with dichloromethane until the washing liquid was colorless, and dried *in vacuo*. Yields, about 30%.

Analyses. Calcd for $C_{25}H_{22}P_2(NCS)_2Ni$: Ni, 10.50; NCS^-, 20.75. Found: Ni, 10.1; NCS^-, 21.1%. This compound can also be obtained from the halo-complexes $[NiX_2(dpm)]$ by exchange with NaSCN in acetone or ethanol-nitromethane solution. However, the samples thus obtained contain variable quantities of solvent (acetone or nitromethane) in the crystal lattice, as indicated by the presence in their vibrational spectra of an absorption at 1720 cm^{-1} for the acetone-solvate, and at 1545 cm^{-1} for the nitromethane-solvate.

Bis(diphenylphosphinoxide)methane, $dpmO_2$. A suspension of I_2 (7.5 g) in chloroform (150 ml) was added to a chloroform solution of bis(diphenylphosphino)methane (5.0 g, in 75 ml). After the reaction mixture had been stirred for 30 min, an aqueous solution of NaOH (3.2 g, in 75 ml) was added and vigorous stirring was continued for an additional 15 min. The chloroform layer was then separated from the aqueous layer and evaporated to dryness under reduced pressure. The solid residue, recrystallized three times from acetone containing 10% triethylorthoformate, gave 4.3 g of pure $dpmO_2$, m.p. 185°.

Infrared absorptions (cm^{-1}): 3055 m, 3025 vw, 3018 sh, 2990 vw, 2940 m, 2872 s, 2738 w, 1590 w, 1485 m, 1438 vs, 1375 m, 1335 w, 1205-1190-1170 (very strong with partly resolved maxima, assigned to the ν(P-O) mode), 1115 m, 1100 sh, 1080 vw, 1020 vw, 790 s, 778 m, 750 w, 735 s, 720 m, 695 s, 688 m, 565 w, 518 s, 510 sh, 492 s, 380 w.

$[Ni(dpmO_2)_3]Cl_2.n(H_2O)$, $[Ni(dpmO_2)_3]Br_2.n(H_2O)$, and $[Ni(dpmO_2)_3]I_2 . n(H_2O)$. The chloride complex was prepared as follows. Solid $NiCl_2 . 6H_2O$ (1 mmole) was added to a warm solution of $dpmO_2$ (3 mmoles) in 95% ethanol (30 ml). The resulting solution was warmed at 50° for 30 min and then allowed to evaporate slowly in air at room temperature until the volume was reduced to about 5 ml. The pale yellow solid which separated was filtered off, washed with a small volume of a chilled 1:1 mixture of acetone and 95% ethanol, and allowed to dry in air for one day. Yields, 85-90%. The bromide and iodide complexes were prepared similarly, using acetone as a solvent. Yields, 80-90%. The compounds thus obtained contained lattice water in quantities that varied with details of the preparation as well as atmospheric conditions. Powdered samples were far more sensitive to changes in humidity than well crystallized samples. The following analytical figures refer to crystalline samples kept in an atmosphere with 50-60 per cent relative humidity at 25°.

Analyses. Calcd for $[Ni(dpmO_2)_3]Br_2 . 6(H_2O)$ = $C_{75}H_{78}O_{12}P_6Br_2Ni$: C, 57.16; H, 4.99; O, 12.19; Ni, 3.73; Br, 10.14; H_2O, 6.86. Found: C, 57.23; H, 4.96; O, 11.76; Ni, 3.5; Br, 10.2; H_2O, 7.1%. (The water content was determined as weight loss in a thermobalance equipped with a dry nitrogen purge.

The vapor evolved was condensed in a cold-trap and identified as pure water by infrared and n.m.r. spectra). Calcd for $[Ni(dpmO_2)_3]Cl_2 . 8(H_2O)$ = $C_{75}H_{82}O_{14}P_6Cl_2Ni$: Ni, 3.85; Cl, 4.65; H_2O, 9.46. Found: Ni, 3.6; Cl, 4.5; H_2O, 10.0%. Calcd for $[Ni(dpmO_2)_3]I_2 . 4(H_2O)$ = $C_{75}H_{74}O_{10}P_6I_2Ni$: C, 55.14; H, 4.34; Ni, 3.59; I, 15.53; H_2O, 4.41. Found: C, 55.9; H, 4.6; Ni, 3.65; I, 15.5; H_2O, 4.8%.

Samples that had been allowed to stand overnight in a 100% humidity environment at 25° did not change in appearance or *d-d* spectra, but their vibrational spectra showed more intense and broader absorptions in the ν(OH) region. In these samples the water content, expressed as number of water molecules per complex entity, approached 12 for the chloride and 8 for the bromide; both samples had an extremely broad ν(OH) absorption extending from 3600 to 3100 cm^{-1}. Under the same conditions the iodide sample contained only 6 H_2O molecules per complex entity, and its infrared spectrum showed a moderately broad, medium ν(OH) absorption centered at 3500 cm^{-1} (half-band width, 300 cm^{-1}). The complexes $[Ni(dpmO_2)_3]X_2 . nH_2O$ were completely dehydrated when placed for 6 hours in a vacuum oven at 40° or when heated above 120°. On further heating the complexes do not melt, but decompose with sharp weight loss above 330°. Both the vibrational and *d-d* electronic spectra of the anhydrous bromide and iodide complexes are identical to those of the hydrated species except for the disappearance of the H_2O absorptions. For the chloride complex however, dehydration is accompanied by a color change from yellow to bluish. The *d-d* electronic spectrum of the bluish substance shows the presence of about 10% $[NiCl_4]^{2-}$, and the vibrational spectrum shows the appearance of the "free" ν(P-O) absorption at 1190 cm^{-1}. Thus. dehydration of $[Ni(dpmO_2)_3]Cl_2 . nH_2O$ causes partial rearrangement to $[Ni(dpmO_2)_3][NiCl_4]$.

The complexes $[Ni(dpmO_2)_3]X_2 . nH_2O$ are quite soluble in a variety of polar solvents, but in solution tend to undergo solvation and ligand scrambling. However, chloroform solutions of $[Ni(dpmO_2)_3]Br_2 . 6H_2O$ and $[Ni(dpmO_2)_3]I_2 . 4H_2O$ have *d-d* spectra superposable with those of the solid complexes.

$[Ni(dpmO_2)_3][NiX_4]$ (X = Cl, Br, I). Solid $dpmO_2$ (3 mmoles) was added to a solution of the nickel(II) halide hexahydrate (2 mmoles) in 30 ml of a mixture of acetone (80%), methanol (10%), and triethylorthoformate (10%). The solution was formed for 10 min and then allowed to evaporate very slowly at room temperature over a period of two days. The crystals that formed (green for the chloro- and bromo-complex, deep red for the iodo-complex) were filtered off, washed with a small volume of acetone containing 10% triethylorthoformate, and dried *in vacuo*. The chloro- and bromo-complexes thus formed contained acetone in the crystal lattice, as shown by the absorptions at ca. 1700 and 1220 cm^{-1} in their infrared spectra. To remove the acetone, these com-

pounds were heated in an oven at 135° for 2 hr (loss of weight, 2 to 4% for different samples of the chloro-complex, 6% for the bromo-complex). The vibrational spectra of the heated products were free from acetone absorptions but otherwise identical to those of the original complexes. The *d-d* electronic spectra of the products with and without acetone were also identical, except that the tail of the near-ultraviolet absorption of the chloro-complex shifted slightly to higher energy upon loss of acetone, resulting in a color change from green to blue. A similar effect was observed for the pseudo-tetrahedral complex $[NiCl_3\{PPh_2CH_2PPh_2(CH_2Ph)\}]$, blue when pure but dark green when containing acetone of solvation.[3]

Analyses. Calcd for $[Ni(dpmO_2)_3][NiI_4]$ = $C_{75}H_{66}O_6P_6I_4Ni_2$: C, 48.06; H, 3.55; O, 5.12; Ni, 6.27; I, 27.08. Found: C, 47.67; H, 3.66; O, 4.5; Ni, 6.2; I, 26.9%. Calcd for $[Ni(dpmO_2)_3]_2[NiCl_4]$ = $C_{75}H_{66}O_6P_6Cl_4Ni_2$: Ni, 7.78; Cl, 9.40. Found: Ni, 7.5; Cl, 9.5%. Calcd for $[Ni(dpmO_2)_3][NiBr_4]$ = $C_{75}H_{66}O_6P_5Br_4Ni_2$: Ni, 6.96; Br, 18.96. Found: Ni, 6.7; Br, 18.7%. The compounds decompose without melting above 330°.

$[Ni(dpmO_3)_2][ZnCl_4]$. The ligand $dpmO_2$ (1 mmole) was dissolved in 30 ml acetone and added to a solution of $NiCl_2 . 6(H_2O)$ (0.3 mmole) and $ZnCl_2$ (0.3 mmole) in 30 ml of methanol containing 10% triethylorthoformate. The clear yellow solution was allowed to evaporate slowly in air, and after one day the yellow crystals that formed were decanted, washed with a small volume of a 1:1 methanol-triethylorthoformate mixture, and dried *in vacuo* at 70°. Yield, 60%.

Analyses. Calcd for $C_{75}H_{66}O_6P_6Cl_4NiZn$: Ni, 3.88; Zn, 4.31; Cl, 9.36. Found: Ni, 3.9; Zn, 3.8; Cl, 9.4%.

Results and Discussion

The monomeric, Four-Coordinate Halo-Complexes, $[NiX_2(dpm)]$ (X = Cl, Br, I). These complexes are readily obtained either by the direct reaction of the dpm ligand with an excess of the anhydrous Ni^{II} halides in a variety of solvents, or by the loss of one dpm ligand from the complex species $[NiX_2(dpm)_2]$. This latter reaction occurs readily under a variety of conditions. The chloro- and bromo-complexes, for example, undergo the change:

$$[NiX_2(dpm)_2] \longrightarrow dpm + [NiX_2(dpm)]$$

simply by recrystallization from appropriate solvents. The complexes $[NiX_2(dpm)]$ with X = Cl, Br, and I closely resemble one another in their physical properties (Table I); the chloro- and bromo-complexes are actually isomorphous, as shown by their identical X-ray powder diffraction patterns.

The complexes $[NiX_2(dpm)]$ are diamagnetic regardless of the method of preparation, thus indicating that Ni^{II} consistently has a singlet ground state. This observation is of interest when compared with the magnetic properties of the analogous complexes $[NiX_2(dpe)]$ (where dpe is the five-atom-ring chelating diphosphine $Ph_2PCH_2CH_2PPh_2$ and X is Cl, Br, and I), which have been variedly described as diamagnetic,[2c] magnetically anomalous[2b] and slightly paramagnetic.[4] The diffuse reflectance electronic spectra of the $[NiX_2(dpm)]$ species consist of a single, very intense absorption at about 20 kK with a very weak shoulder on the low energy side, a spectral pattern fairly diagnostic of low-spin Ni^{II} in planar complexes.[5a] The spectra of the $[NiX_2(dpm)]$ species are in fact almost identical to those of the corresponding $[NiX_2(dpm)_2]$ complexes of monodentate dpm and closely resemble those reported[2c] for the chelate complexes $[NiX_2(dpe)]$, containing the five-atom chelating diphosphine, $Ph_2PCH_2CH_2PPh_2$. When the $[NiX_2(dpm)]$ complexes are dissolved in dichloromethane, in which they are moderately soluble, their *d-d* electronic spectra remain unchanged except for the minor frequency shifts commonly observed for planar complexes of d^8 metal ions, and follows Beer's law even at high dilutions. Thus the $[NiX_2(dpm)]$ species retain their singlet ground state in solution and show no tendency to give singlet-triplet equilibria similar to those observed[2c] for solutions of the closely related complexes $[NiX_2(dpp)]$, where dpp is the six-atom-ring chelating diphosphine, $Ph_2PCH_2CH_2CH_2PPh_2$.

The vibrational spectra of the three species $[NiX_2(dpm)]$ are identical to one another except for the presence in the chloro-complex of a strong and slightly split absorption at 305-300 cm^{-1}, arising from the Ni-Cl stretching modes.[6,7] The entire pattern of the spectra of the $[NiX_2(dpm)]$ species resembles closely that of the free dpm ligand[8] and of the $[NiX_2(dpm)_2]$ complexes in which dpm is monodentate, except for the presence of a new medium-strong band at 535-540 cm^{-1}. We have also observed this "new" band in the spectra of the bischelate complexes $[M(dpm)_2]Cl_2$ of planar Pd^{II} and Pt^{II}, but not in the corresponding zerovalent complexes $[M(dpm)_2]$[2a] which again presumably contain chelated dpm but have a pseudo-tetrahedral geometry.

On the basis of all these data, the $[NiX_2(dpm)]$ complexes can be confidently assigned a monomeric formula, with dpm acting as a chelate rather than a bridging ligand. This is confirmed by the mass spectrum of the iodo-complex, in which the heaviest observed particle corresponds to the $[NiI_2(dpm)]$ complex itself. For the chloro- and bromo-complexes the parent species could not be detected but the fragmentation pattern still indicates the presence of chelated dpm, the heaviest fragment being the [Ni(dpm)] moiety.

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Table I. Some Properties of Ni^{II} Complexes of Bis(diphenylphosphino)methane

Complex[a]	Color and Crystal Form	Dec. Temp. in N_2 atm.[b]	Magnetic Behavior[c]	*d-d* Electronic Absorption, kK		
				Solid, Reflectance[d]	CH_2Cl_2 Soln.[e]	CH_2Cl_2 Soln.[e,f] with added diphosphine
[$NiCl_2$(dpm)]	brown needles	260°	diam.	20.5	20.4 (1580)	20.9 (1710)
[$NiBr_2$(dpm)]	red-brown needles	275°	diam.	20.0	20.1 (1630)	20.3 (1900)
[NiI_2(dpm)]	purple needles	300°	diam.	19.5 13.0 sh[j]	18.4 (2100) 13.1 sh	18.6 (2200)
[Ni_2I_4(dpm)$_2$]	olive-green prisms	325°	diam.	23.8 17.9 12.9 10.0 sh	23.8[h] 17.9[k] 12.9 (~2000)	18.6 (2200)
trans-[Ni(NCS)$_2$(dpm)$_2$]	orange-yellow needles	168°[g]	diam.	25.0 19.2 sh	25.0 22.2	25.1 (8000)
[Ni_2(NCS)$_4$(dpm)$_2$]	brick-red prisms	300°	diam.	24.4 18.8	24.4 sh 22.7	25.1 (8000)

[a] dpm = $Ph_2PCH_2PPh_2$. [b] The diphosphine sublimes. [c] For solid samples at room temperature. [d] Reported values are mid-points of rather broad asymmetric bands. [e] Reported values are maxima of symmetric bands. Molar extinction coefficients are given in parentheses. [f] All dichloromethane spectra with added diphosphine are identical with those of the corresponding [NiX_2(dpm)$_2$] species. The molar extinction coefficients decrease with time. [g] The compound melts sharply. [h] Absorption ill-resolved from strong band at higher energy. [k] Absorption arising from some monomeric [NiI_2(dpm)]. [j] Absorpthion arising from some dimeric [Ni_2I_4(dpm)$_2$].

The five-Coordinate Dimer, [Ni_2I_4(dpm)$_2$]. The chelate monomeric iodo-complex, [NiI_2(dpm)], undergoes an unexpected change when recrystallized from dichloromethane. If a dichloromethane solution containing the purple [NiI_2(dpm)] species is diluted with a small volume of triethylorthoformate and allowed to evaporate very slowly almost to dryness, a solid separates that consists of very small but well formed greenish-black prisms. The same change occurs when a suspension of the chelate complex [NiI_2(dpm)] in acetone is warmed gently for several hours. The new olive-green substance still has an analytical composition corresponding to NiI_2 . dpm, and thus is obviously an isomer of the chelate purple complex. The olive-green compound is virtually insoluble in most solvents, although it does dissolve very slightly in dichloromethane. The compound is diamagnetic and its vibrational spectrum still shows the absorptions of the bis(diphenylphosphino)methane ligand, but the medium-strong band at 535-540 cm^{-1}, characteristic of the four-atom chelating diphosphine in its planar complexes, is no longer present. The electronic spectrum of the olive-green complex (Figure 1) in the crystalline state shows several strong though ill-resolved absorptions extending throughout the entire visible region, and thus differs markedly from the characteristic pattern of four-coordinate planar Ni^{II}. Rather, the spectrum of the olive-green complex resembles the spectral pattern of some low-spin five-coordinate complexes of Ni^{II} iodide with polydentate "hybrid ligands", reported by Sacconi and co-workers as having a distorted square pyramidal geometry.[9] The similarity is even more evident for the spectra of freshly prepared dichloromethane solutions at low temperature (—10°), and taken in conjunction with other properties clearly identifies the olive-green compound as an iodo-bridged, five-coordinate dimer with chelating diphosphine ligands (Formula I).

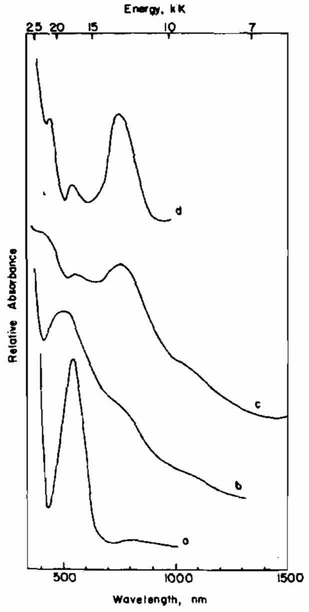
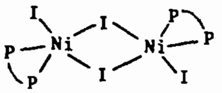


Figure 1. *d-d* electronic spectra of: *a*, [NiI_2(dpm)] in dichloromethane solution; *b*, [NiI_2(dpm)] solid (reflectance); *c*, [Ni_2I_4(dpm)$_2$] solid (reflectance); *d*, [Ni_2I_4(dpm)$_2$] in dichloromethane solution at —10°.



I

It may be pointed out that this formula also appears to be the most likely on the basis of chemical considerations: An iodo-bridged formula, rather than one involving bridging diphosphine, is suggested by the observation that the chloro- and bromo-chelate complexes do not form "insoluble isomers" under any of the conditions tried. Furthermore, it is well

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(9) R. Morassi and L. Sacconi, *J. Chem. Soc.*, *A*, 1487 (1970), and references therein.

known that for the heavier d^8 metal ions, Pd^{II} and Pt^{II}, iodo-bridged complexes are far easier to form and also far more stable than chloro and bromo-bridged complexes.[10] Although we are unaware of any well-established example of iodo-bridged Ni^{II} complexes, it is reasonable to assume that the trend existing for Pd^{II} and Pt^{II} may also extend to Ni^{II} in a low-spin electron configuration. However, in this example Ni^{II} differs from its heavier homologs in that it forms a five-cordinate rather than a four-coordinate dimeric species.

The spectral study of the dichloromethane solutions of the olive-green dimeric complex $[Ni_2I_4(dpm)_2]$ also offers another interesting aspect. If the chilled solution is allowed to warm up to room temperature or if the solution is prepared directly at room temperature, the color is no longer olive-green but has a tinge of purple. In fact the electronic spectrum now shows a fairly intense absorption due to the purple four-coordinate monomer, superposed on the two characteristic absorptions of the olive-green five-coordinate dimer. As time passes, the two absorptions of the dimer gradually decrease in intensity and finally disappear, while the absorption of the monomer reaches a maximum intensity which then remains constant thereafter. The change of these spectra with time, shown in Figure 2, clearly indicates that the five-coordinate dimer and the four-coordinate monomer are the only two chromophores present in this solution, and that the monomer is the more stable form although a small concentration of the dimer may still be present in solution at equilibrium.

The Thiocyanato Complexes. The results obtained with the chloro-, bromo-, and iodo-complexes lead us to investigate the reaction of the dpm ligand with Ni^{II} thiocyanate. It is well known that the NCS^- ion is a strong bridging ligand which favors the formation of very stable NCS-bridged dimeric complexes[11] for the heavier low-spin d^8 metal ions—Rh^I, Pd^{II}, Pt^{II}—and may be expected to behave similarly also with low-spin Ni^{II}. Furthermore when acting as a monodentate ligand, the NCS^- ion can be either N-bonded or S-bonded, depending not only on the "soft-hard" character of the metal ion, but also on the strength and steric requirements of the other partner ligands present in the complex.[12] For example, in a series of Pd^{II} complexes of chelated diphosphines, of the type $[Pd(NCS)_2\{Ph_2P(CH_2)_nPPh_2\}]$, the NCS^- groups have been found[13] to be S-bonded for n = 1, both N-bonded and S-bonded for n = 2, and only N-bonded for n = 3.

The direct reaction of Ni^{II} thiocyanate with the diphosphine dpm in alcohol solution yields a beautifully crystalline red-orange compound, which has the analytical composition $Ni(NCS)_2 . 2dpm$. This compound is diamagnetic and its electronic spectrum (reflectance, Figure 3) shows one strong band at 25.0 kK with a shoulder at 19.2 kK and is virtually identical to that observed for a series of planar complexes of the type *trans*-$[Ni(NCS)_2(PR_3)_2]$.[14] The vibrational spectrum shows, in addition to the usual pattern of the dpm ligand, a very strong and sharp single ab-

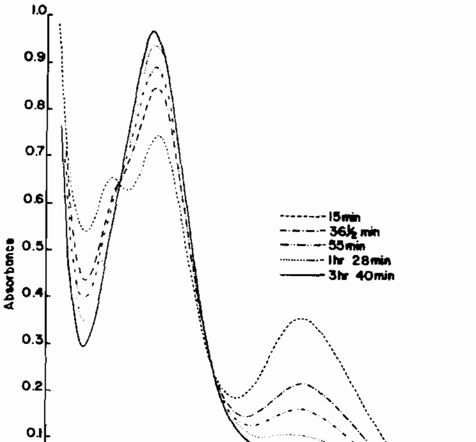

Figure 2. Variation with time of the *d-d* electronic spectrum of a solution obtained by dissolving $[Ni_2I_4(dpm)_2]$ in dichloromethane at room temperature ($M = 0.460 \times 10^{-3}$). The absorptions at 775 and 475 nm are due to the five-coordinate dimer $[Ni_2I_4(dpm)_2]$, whereas the absorption at 540 nm is due to the four-coordinate monomer $[NiI_2(dpm)]$. The first spectrum was recorded 15 min after initial contact of the solid solute with the solvent, time being required to attain complete dissolution.

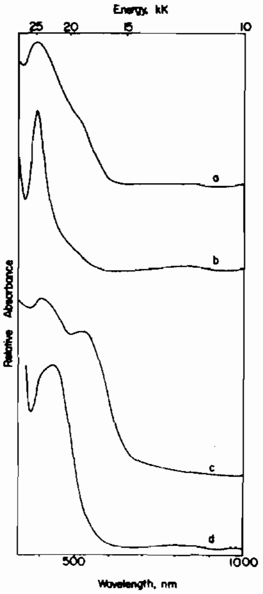

Figure 3. *d-d* electronic spectra of: *a*, *trans*-$[Ni(NCS)_2(dpm)_2]$ solid (reflectance); *b*, *trans*-$[Ni(NCS)_2(dpm)_2]$ in dichloromethane solution with added diphosphine; *c*, $[Ni_2(NCS)_4(dpm)_2]$ solid (reflectance); *d*, solution obtained by shaking solid $[Ni_2(NCS)_4(dpm)_2]$ in dichloromethane for several hours.

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[10] J. Chatt and L.M. Venanzi, *J. Chem. Soc.*, 3858 (1955).

[11] J. Chatt and F.A. Hart, *J. Chem. Soc.*, 1416 (1961).

[12] (a) D.W. Meek, P.E. Nicpon, and V.I. Meek, *J. Am. Chem. Soc.*, *92*, 5351 (1970). (b) G. Beran and G.J. Palenik, *Chem. Comm.*, 1354 (1970).

[13] G. Beran, A.J. Carty, P.C. Chieh, T.W. Ng, G.J. Palenik, and H.A. Patel, paper presented at the XIV I.C.C.C., Toronto, Canada, June 1972.

[14] M.C. Browing, J.R. Mellor, D.J. Morgan, S.A.J. Pratt, L.E. Sutton, and L.M. Venanzi, *J. Chem. Soc.*, 693 (1962) and references therein

sorption at 2080 cm^{-1} (C-N stretching mode) and a medium fairly sharp absorption at 865 cm^{-1} (C-S stretching mode). The relatively high frequency of the ν(C-S) absorption is clearly diagnostic of N-bonded thiocyanate. Thus, on the basis of its magnetic and spectral properties, the red-orange complex may be formulated as the planar *trans*-[Ni(NCS)$_2$(dpm)$_2$], containing monodentate dpm.

The *trans*-[Ni(NCS)$_2$(dpm)$_2$] complex is stable toward air and moisture at room temperature, and melts with decomposition at 168° in the same range as the halo-complexes of the type [NiX$_2$(dpm)$_2$]. The *trans*-[Ni(NCS)$_2$(dpm)$_2$] complex is moderately soluble in non-donor solvents; however, the electronic spectra of its solutions differ somewhat from the spectrum of the solid complex indicating partial dissociation to one or more other planar species. This dissociation is repressed when some diphosphine ligand is added to the solution, and the spectrum then becomes identical to that of the solid (Figure 3).

An interesting change is observed when the solid *trans*-[Ni(NCS)$_2$(dpm)$_2$] is treated with a small volume of dichloromethane without added diphosphine. At first the red-orange needles dissolve completely, giving a red-orange solution; almost immediately however, the solution becomes cloudy and a different solid begins to separate as small brick-red prisms. This new substance, which is only very sparingly soluble in dichloromethane and is insoluble in most other solvents, is diamagnetic and has the analytical composition Ni(NCS)$_2$. dpm, thus corresponding in stoichiometry to the halo-complexes of chelating dpm. The vibrational spectrum of the brick-red Ni(NCS)$_2$. dpm shows the characteristic pattern of the dpm ligand, and in addition has two strong sharp and well resolved C-N stretching absorptions at 2085 and 2055 cm^{-1}, as well as a medium C-S stretching absorption at 865 cm^{-1} (Figure 4). Thus the vibrational spectrum is consistent with either a monomeric chelated formula involving two N-bonded NCS$^-$ groups in *cis* positions ,or with a dimeric formula involving both bridging and terminal (N-bonded) NCS$^-$ groups. The almost complete lack of solubility of the Ni(NCS)$_2$. dpm complex, which contrasts sharply with the behavior of the monomeric chelate halo-complexes [NiX$_2$(dpm)] and of the related monomeric chelate species [Ni(NCS)$_2$(dpe)], obviously suggests a dimeric structure. Again, as for the dimeric iodo-complex, the electronic spectrum of [Ni$_2$(NCS)$_4$(dpm)$_2$] shows two intense although ill-resolved bands at 24.4 and 18.8 kK, strongly suggesting a five-coordinate formula, II.

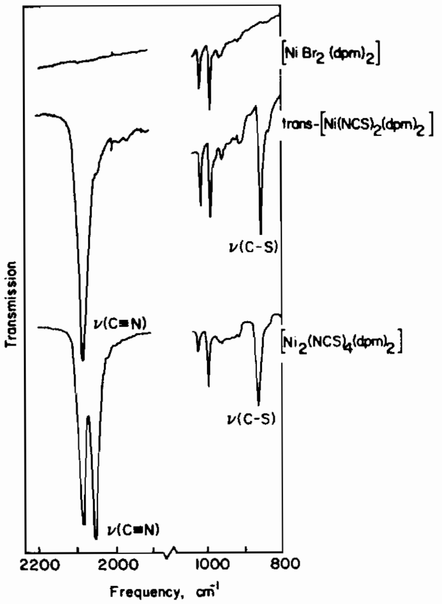
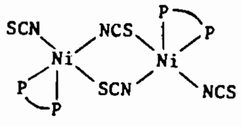


Figure 4. The C≡N and C–S stretching vibrations of the *trans*-[Ni(NCS)$_2$(dpm)$_2$] and [Ni$_2$(NCS)$_4$(dpm)$_2$] complexes.



II

The brick-red crystalline [Ni$_2$(NCS)$_4$(dpm)$_2$] although insoluble in most solvents on first contact, does dissolve very sparingly when stirred in dichloromethane for several hours. The spectrum of the resulting yellow solution shows a single slightly asymmetric absorption at 22.7 kK, indicative of a new four-coordinate planar species, very likely the chelated monomer resulting from the dimer by splitting of the NCS-bridges.

Air-Oxidation of the Chelate Complexes [NiX$_2$(dpm)]. The chelate complexes [NiX$_2$(dpm)] have a remarkable thermal stability. In a dry nitrogen atmosphere they can be heated without melting or decomposition up to about 260° (the temperature for each halo-complex is listed in Table I); at higher temperatures the coordinated phosphine begins to vaporize slowly. The high thermal stability of the chelate complexes [NiX$_2$(dpm)] is particularly interesting when compared to the behavior of the complexes of monodentate dpm, [NiX$_2$(dpm)$_2$], which melt with decomposition in the range 110-150°. The chelate complexes [NiX$_2$(dpm)] are also stable up to about 220° in the presence of oxygen or air. Above this temperature however, they begin to react: for example, between 225° and 270° the bromo-complex [NiBr$_2$(dpm)] slowly changes color from deep red-brown to green, while at the same time its mass increases by a quantity corresponding to the uptake of two oxygen atoms per molecule of complex. The vibrational spectrum of the green product thus formed is completely different from that of the original complex, and the appearance of a new intense absorption at 1155 cm^{-1} strongly suggests the presence of metal-coordinated P-O groups. In fact, from the entire pattern of the vibrational spectrum and also from the *d-d* electronic spectrum, the green oxidation product is clearly identified as the ionic complex [Ni(dpmO$_2$)$_3$][NiBr$_4$], which will be discussed later together with other complexes of the chelating diphosphine-dioxide ligand dpmO$_2$.

The "decomposition" of [NiBr$_2$(dpm)] when heateed in air above 225° thus consists essentially of the oxidation of the chelated diphosphine to its chelated

Table II. Some Properties of Ni^{II} Complexes of Bis(diphenylphosphinoxide)methane

Complex [a]	Color and Crystal Form	*d-d* Electronic Absorptions-[b] (kK) and Assignments								
		Octahedral $[Ni(dpmO_2)_3]^{2+}$ $^3A_{2g}(F) \rightarrow$					Tetrahedral $[NiX_4]^{2-}$ $^3T_1(F) \rightarrow$			
		$^3T_{1g}(P)$	$^1T_{1g}$	^1E_g	$^3T_{1g}(F)$	$^3T_{2g}F$	^1D	$^3T_1(P)$	^1E	$^3A_2(F)$
$[Ni(dpmO_2)_3]Cl_2 . nH_2O$ [c]	yellow small needles	23.1	20.0 sh	14.4	12.1	7.4				
$[Ni(dpmO_2)_3]Br_2 . nH_2O$ [d]	yellow small needles	23.2	20.0 sh	14.4	12.2	7.4				
$[Ni(dpmO_2)_3]I_2 . nH_2O$ [e]	yellow prisms	23.2	20.0 sh	14.4	12.3	7.4				
$[Ni(dpmO_2)_3][NiCl_4]$	blue [g] prisms	23.2	20.0 sh	[h]	[h]	[h]	20.0 sh	15.0 14.1	11.8	7.4
$[Ni(dpmO_2)_3][NiBr_4]$	green prisms	23.2		[h]	[h]	[h]	18.0 sh	14.2 13.2	10.8	7.3
$[Ni(dpmO_2)_3][NiI]_4$	red-brown prisms	[i]		[h]	[h]	[h]		13.6 sh 12.5 11.1		7.4
$[Ni(dpmO_2)_3][ZnCl_4]$	yellow prisms	23.2	20.4 sh	14.4	12.3	7.4				

[a] $dpmO_2$ = bis(diphenylphosphinoxide)methane = $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)_2$. [b] Values reported are band maxima from diffuse deflectance spectra. [c] n varies between ~4 and ~12 depending on preparation and humidity of environment. Anhydrous samples usually are impure by small amounts of $[Ni(dpmO_2)_3][NiCl_4]$. [d] n varies between 0 (samples dried in vacuo at 40°) and 7 to 8 (samples kept in a 100% humidity environment at 25°). [e] n varies between 0 (sample dried in vacuo at 40°) and ~6 (sample kept in a 100% humidity environment at 25°). [f] Well-defined shoulder on tail of strong absorption at higher energy. [g] Samples containing acetone in the crystal lattice are greenish. [h] Obscured by strong tetrahedral absorption in this region. [i] Obscured by extremely strong absorption with maxima at 25.0 and 19.0 kK.

dioxide, with rearrangement to a species of different stereochemistry. The observation that for $[NiBr_2(dpm)]$ the oxygen uptake begins some 50° below the onset of vaporization of the diphosphine strongly suggests that the oxidation process indeed involves the coordinated dpm ligand. This very unusual reaction is particularly significant in view of the current interest in the reactivity of coordinated ligands and is being further investigated.

The other chelate halo-complexes, $[NiCl_2(dpm)]$ and $[NiI_2(dpm)]$, also behave in a similar manner and when heated in air between 220° and 270° slowly oxidize forming as the chief products $[Ni(dpmO_2)_3][NiCl_4]$ and $[Ni(dpmO_2)_3][NiI_4]$ respectively. The thermogravimetric study of these reactions showed a mass increase lower than expected, but this is not surprising since for both the chloro- and the iodo-complex the oxygen uptake begins nearly at the same temperature as the vaporization of diphosphine, and for the iodo-complex the situation is further complicated by the tendency of the Ni-bonded iodo-ligands to oxidize. (It may be recalled that nickel(II) iodide itself gives off iodine vapor in air even at room temperature.)

Complexes of Nickel(II) Halides With the Chelating Diphosphine-dioxide Ligand, $dpmO_2$. The observed air-oxidation of the diphosphine complexes $[NiX_2(dpm)]$ led us to investigate for comparison the complexes formed directly by reaction of the nickel(II) halides with the diphosphine-dioxide, $Ph_2P(O)CH_2P(O)Ph_2$ ($dpmO_2$). Depending on the nickel-ligand mole ratio used in the preparation, two series of complexes were obtained, having stoichiometry $NiX_2 . 3dpmO_2 . nH_2O$ and $2NiX_2 . 3dpmO_2$, respectively (X = Cl, Br, I).

The compounds of stoichiometry $NiX_2 . 3dpmO_2 . nH_2O$ (where the value of n depends upon the halide as well as the experimental conditions) are yellow crystalline substances. Their *d-d* electronic spectra, shown in Figure 5 and Table II, are independent of both the halide X and the number of H_2O molecules, and clearly indicate that in all these compounds Ni^{II} is present as a single octahedral species with a relatively weak crystal field. The vibrational spectra of these three halide compounds of stoichiometry $NiX_2 . 3dpmO_2 . nH_2O$ are also identical, and show a pattern almost unchanged from that of the "free" $dpmO_2$ ligand except for the shift of ν(P-O) absorption from 1190 to 1155 cm^{-1} (Figure 6). In addition, the vibrational spectra show a medium very broad band centered at 3500 cm^{-1} and a weak broad band at 1650 cm^{-1}, which arise respectively from the ν(OH)

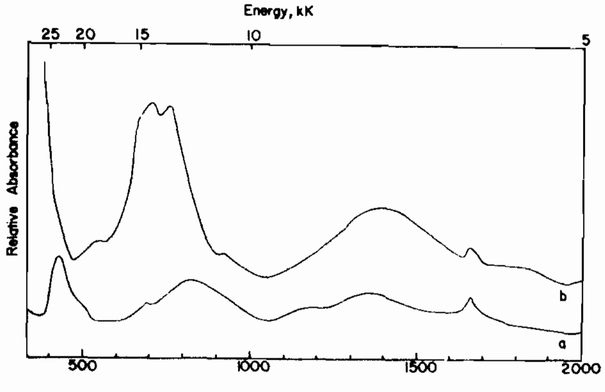


Figure 5. *d-d* electronic spectra of: *a*, $[Ni(dpmO_2)_3]Br_2 . nH_2O$ solid (reflectance); *b*, $[Ni(dpmO_2)_3][NiBr_4]$, solid (reflectance).

and$\delta(OH_2)$ modes and are clearly diagnostic of rather disordered lattice water.

The compounds $NiX_2 . 3dpmO_2 . nH_2O$ readily lose their water when heated to about 110°C, or even at 40° under vacuum. For the bromide and iodide complexes, complete dehydration does not involve any change in the coordination sphere of Ni^{II}, since no change is observed in either the *d-d* electronic or the vibrational spectra of the complexes—except for the disappearance of the characteristic H_2O absorptions. (For the chloride complex, some rearrangement takes place upon dehydration as described in the *Experimental Section.*) On the basis of all these data, the compounds of stoichiometry $NiX_2 . 3dpmO_2 . nH_2O$ are formulated as the hydrated ionic species $[Ni(dpmO_2)_3]X_2 . nH_2O$, with the tris-chelate cation having a high-spin octahedral geometry. It is interesting to mention that these ionic compounds, both anhydrous and hydrated, are somewhat soluble in chloroform. The *d-d* electronic spectra of the resulting solutions are identical to those of the solid complexes, showing that the $[Ni(dpmO_2)_3]^{2+}$ cation is quite stable in appropriate solvents.

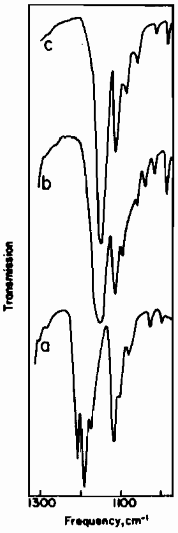


Figure 6. The P-O stretching vibration in: *a*, the ligand $dpmO_2$; *b*,$[Ni(dpmO_2)_3]Br_2 . nH_2O$; *c*, $[Ni(dpmO_2)_3][NiBr_4]$.

For the series of compounds of stoichiometry $2NiX_2 . 3dpmO_2$, the vibrational spectra are virtually identical to those of the anhydrous $[Ni(dpmO_2)_3]X_2$ salts, and the *d-d* electronic spectra (Table II and Figure 5) clearly show the characteristic absorptions of the tetrahedral $[NiX_4]^{2-}$ anions superposed upon the weaker absorptions of the octahedral $[Ni(dpmO_2)_3]^{2+}$ cation. Thus, these complexes are formulated as the ionic species $[Ni(dpmO_2)_3][NiX_4]$. This structure is further confirmed by comparison of $[Ni(dpmO_2)_3]$-$[NiCl_4]$ with the X-ray isomorphous complex $[Ni(dpmO_2)_3][ZnCl_4]$, which is yellow and has a *d-d* spectrum identical to that of the anhydrous $[Ni(dpmO_2)_3]Br_2$ salt.

These results indicate that $dpmO_2$ tends to coordinate to Ni^{II} forming the tris-chelate octahedral complex $[Ni(dpmO_2)_3]^{2+}$, even when an excess of nickel(II) halide is present. In this respect $dpmO_2$ resembles the mono- and bi-dentate N-oxide and S-oxide ligands—e.g., pyridine-N-oxide,[15] dipyridyl-N,N'-dioxide,[16] dimethylsulfoxide,[17] which all form readily the octahedral $[NiO_6]^{2+}$ species—rather than the monodentate P-oxide and As-oxide ligands—e.g., triphenylphosphinoxide and triphenylarsinoxide, which favor the formation of pseudo-tetrahedral $[NiX_2O_2]$ species.[18a,b]

It is interesting to observe, however, that the lowering of the P-O stretching frequency of $dpmO_2$ upon coordination in the $[Ni(dpmO_2)_3]^{2+}$ complex ($\Delta\nu_{(P\text{-}O)} = -35$ cm^{-1}) is identical with that reported for triphenylphosphinoxide in the tetrahedral $[NiCl_2(Ph_3PO)_2]$ complex ($\Delta\nu_{(P\text{-}O)} = -35$ cm^{-1}),[18a] indicating that at least from the viewpoint of the ligand the oxygen-to-nickel bonding in these two complexes is quite similar. It is also interesting to observe that the crystal field parameters of the $[Ni(dpmO_2)_3]^{2+}$ complex ($Dq = 0.74$, $B = 0.89$ kK), indicate that the O-donor atoms of $dpmO_2$ are slightly weaker ligands than the O atoms of pyridine-N-oxide ($Dq = 0.84$, $B = 0.90$ kK) and dimethylsulfoxide ($Dq = 0.77$, $B = 0.91$ kK), although the Racah parameters are virtually the same.[17,5b] The O atoms of a phosphine-oxide ligand thus occupy a position only slightly higher than the Cl^- ion in the spectrochemical series of octahedral Ni^{II}. If this result is logically extended to tetrahedral Ni^{II}, it becomes understandable that the *d-d* electronic spectrum of the complex $[NiCl_2(Ph_3PO)_2]$ is virtually indistinguishable from that of $[NiCl_4]^{2-}$ (showing no reduction of symmetry from T_d to C_{2v}), whereas the spectra of the bromo- and iodo-complexes, $[NiX_2(Ph_3PO)_2]$ differ quite markedly from those of the corresponding $[NiX_4]^{2-}$ ions.

The marked tendency of $dpmO_2$ to give the octahedral species $[Ni(dpmO_3)_2]^{2+}$ under a variety of experimental conditions very likely results from a balance of electronic and steric factors. The formation of the three six-atom chelate rings, which may be expected to be nearly planar and allow some π-electron delocalization, undoubtedly plays an important role in the stabilization of this complex species. Also important is the contribution of the crystal field stabilization energy, which for Ni^{II} is appreciably greater in an octahedral than in a tetrahedral field of comparable ligands. In this respect it is significant that reaction mixtures containing $dpmO_2$ Ni^{II}, Zn^{II}, and Cl^- in a 3:1:1:4 mole ratio consistently yielded the complex $[Ni(dpmO_3)_2][ZnCl_4]$, with never a trace of $[Zn(dpmO_3)_2][NiCl_4]$ being formed although the cation $[Zn(dpmO_2)_3]^{2+}$ was itself readily obtained[19] from Zn^{II} and $dpmO_2$. This is a striking example of the directing influence of crystal field effects on the synthesis of mixed-metal complexes.

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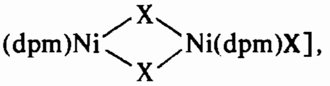
(19) C. Ercolani, J.V. Quagliano, and L.M. Vallarino, unpublished results.

Conclusions

The present work shows that the diphosphine dpm, $Ph_2PCH_2PPh_2$, readily forms chelate complexes with low-spin Ni^{II}, as it does with the heaviest d^8 metal ions, Pd^{II} and Pt^{II}. The four-atom chelate ring present in these complexes must obviously impose a drastic strain on the bond angles of both the ligand and the metal—for example, the P-Pd-P angle of chelating dpm has been found to be 75 degrees[13]—yet the $[NiX_2(dpm)]$ complexes are remarkably stable both in the solid state and in solution. In fact, both the overall stability and the ligand field strength of the four-atom-ring chelate complexes $[NiX_2(dpm)]$ resemble closely those of the corresponding complexes of the diphosphine $Ph_2PCH_2CH_2PPh_2$, which forms almost strainless five-atom chelate rings with planar metal ions. However, the strain of the Ni-dpm chelate ring is probably responsible for the very unusual air-oxidation of the Ni^{II}-coordinated dpm ligand at high-temperature, which results in the formation of the ionic complexes $[Ni(dpmO_2)_3][NiX_4]$ containing almost strainless Ni^{II}-diphosphine-dioxide chelated rings.

The chelated dpm ligand also appears to be unique in its tendency to favor the formation of low-spin five-coordinate dimeric complexes of the type [X-  $[\mathrm{X}\text{-}(\mathrm{dpm})\mathrm{Ni}\overset{\mathrm{X}}{\underset{\mathrm{X}}{\diamond}}\mathrm{Ni}(\mathrm{dpm})\mathrm{X}]$, where X is I or NCS. Although these five-coordinate dimeric complexes are extremely stable in the solid state, in solution they revert completely to the monomeric four-coordinate planar form This behavior is often observed[9] for five-coordinate low-spin Ni^{II} species in which a square pyramidal structure is attained by formation of an elongated bond with a "weaker" donor atom perpendicularly to the plane of the four other "stronger" ligands.

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