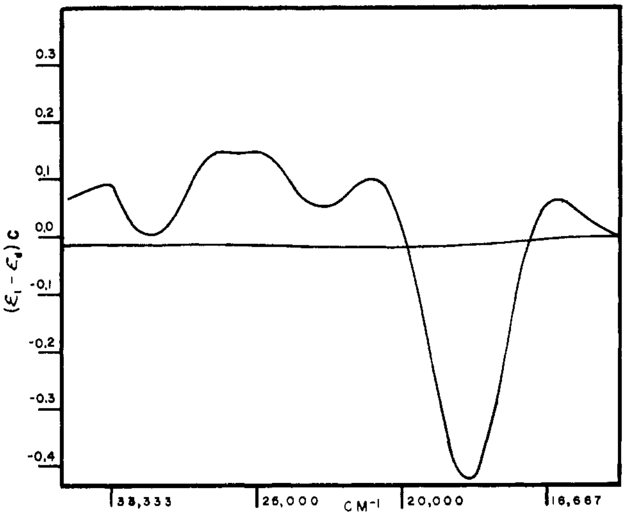

Figure 5.—Circular dichroism spectrum of Co(EDDS)$^-$ in water.

therefore make a larger contribution to the equatorial field. It is tempting to use the foregoing results from the electronic spectra to support this view but any such argument is dulled by the unknown effect of changing from tertiary to secondary nitrogen donors between EDTA and EDDS. Furthermore, data available for complexes containing isolated five- and six-membered rings, notably *cis*-Co($NH_2CH_2COO)_3$[32] and *cis*-Co($NH_2CH_2CH_2COO)_3$,[25] would suggest that *Dq* values for the six-membered rings are smaller (Table IV). However a strict comparison of the effects of ring size in complexes of simple amino acids with those of EDTA and EDDS might well be inappropriate. In the latter two complexes a change in ring size has been accomplished without addition of "extra" atoms thereby minimizing any change in nonbonding interactions. It seems to these authors that case I is the most likely choice. Any argument favoring case II must be largely predicated on the chirality rules of Legg and Douglas, in that both $(+)_{546}$-Co(EDTA)$^-$ and Co(EDDS)$^-$ exhibit a negative rotation in the major low-energy band (see Figure 2).[31] Clearly an X-ray diffraction study is required to fix securely the absolute configuration of Co(EDDS)$^-$.

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Dibromotris(trimethylphosphine)nickel(II)

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The reaction of nickel bromide and 3 mol of trimethylphosphine yields the five-coordinate complex $Ni(P(CH_3)_3)_3Br_2$. The rich electronic spectrum of the complex contains both ligand field and charge-transfer absorption bands and is compatible with a trigonal-bipyramidal structure for the ground state. The presence of two moderately intense ligand field bands indicates that the molecule is distorted toward a tetragonal pyramid in the excited states derived from a^1E'. Allowed Br→Ni(II) charge-transfer bands are observed at 26,200 and 40,400 cm^{-1}, whereas an allowed $P(CH_3)_3$→Ni(II) band is found at 36,400 cm^{-1}.

Introduction

Numerous investigations have been carried out on the reaction of nickel(II) compounds with various trialkyl- and triarylphosphines.[2-8] The products in many cases have been four-coordinate complexes containing two phosphine molecules; notable examples include the square-planar $Ni(P(C_2H_5)_3)_2Br_2$[9] and the tetrahedral $Ni(P(C_6H_5)_3)_2Cl_2$[10] complexes.

Beg and Clark have reported[11] that the direct reaction of trimethylphosphine with nickel(II) salts in a 2:1 mole ratio in a sealed tube yields diamagnetic $Ni(P(CH_3)_3)_2X_2$ (X^- = Cl^-, Br^-, I^-, SCN^-) complexes. Jensen and coworkers, however, in their investigations of nickel(II)–phosphine complexes, noted a difference in the behavior of trimethylphosphine as compared to the higher trialkylphosphines.[12] Using nickel chloride, only red $Ni(P(CH_3)_3)_2Cl_2$ was isolated, but with nickel bromide an almost black compound was produced which analyzed for 3 mol of phosphine. It was tentatively suggested that the dark compound might be a mixture of the four-coordinate complex containing two phosphine molecules and a six-coordinate form containing four phosphine molecules. These investigators also re-

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ported that the trimethylphosphine complexes were oxidized by atmospheric oxygen to compounds containing trivalent nickel.

This paper presents the preparation and characterization of the five-coordinate complex $Ni(P(CH_3)_3)_3Br_2$, which appears to be reasonably air stable. The electronic spectrum of the complex is compared with the electronic energy levels expected for a model D_{3h} complex and some tentative structural conclusions are drawn.

Experimental Procedures

Preparation of Compounds. Trimethylphosphine, $P(CH_3)_3$.—Trimethylphosphine was prepared as described by Jensen, *et al.*,[12] and collected as the silver iodide complex. This compound should be stored in the dark, preferably in a cold room. The phosphine was conveniently regenerated from the complex by heating the solid compound in a microdistillation unit in a nitrogen atmosphere at 100–150° with an oil bath. The over-all yield of distilled $P(CH_3)_3$ was 40%.

Dibromotris(trimethylphosphine)nickel(II), $Ni(P(CH_3)_3)_3Br_2$.—A 4.0-g amount of $P(CH_3)_3$ (0.053 mol) was added under nitrogen to a deaerated 1-butanol solution of 3.27 g of $NiBr_2 \cdot 6H_2O$ (0.01 mol) at 25° while stirring. The solution turned deep blue immediately, and dark crystals were deposited when the solution was cooled overnight at $-10°$. These were collected on a filter, recrystallized from dichloromethane, and dried in a desiccator over $CaCl_2$; yield, 60%. *Anal.* Calcd for $Ni(P(CH_3)_3)_3Br_2$: C, 24.22; H, 6.10; Br, 35.79. Found: C, 23.82; H, 6.06; Br, 35.49.

Physical Measurements.—Electronic spectra were measured on a Cary Model 14 recording spectrophotometer, using spectral grade dichloromethane as solvent. Magnetic susceptibility measurements on solid samples were made using the Gouy method with $Hg[Co(NCS)_4]$[13] as calibrant; the data were checked with a Foner magnetometer. Molecular weight data were obtained by osmometry using chloroform as solvent.

Characterization of $Ni(P(CH_3)_3)_3Br_2$

The measured molecular weight of 424 (calculated, 447) and the analytical data are consistent with a monomeric complex of the formula $Ni(P(CH_3)_3)_3Br_2$. Our spectroscopic data show that the four-coordinate complex[11] $Ni(P(CH_3)_3)_2Br_2$ is not present and thus are incompatible with the formulation as a mixture of four- and six-coordinate species. The complex is diamagnetic; $\chi_m^{\text{uncor}} = -248 \times 10^{-6}$ cgsu. Standard diamagnetic corrections give $\mu_{\text{eff}} = 0.30$ BM, consistent with a small temperature-independent paramagnetism. The complex dissolves readily in benzene, dichloromethane, and acetone to give deep blue solutions. These solutions tend to decompose on standing, especially in the presence of light. The solid complex is not readily oxidized by air, but evolves $P(CH_3)_3$ at room temperature over a period of several months and becomes red, forming the known square-planar complex $Ni(P(CH_3)_3)_2Br_2$; dissolution of the five-coordinate complex in hexane or carbon tetrachloride also gives the red, four-coordinate species. Dichloromethane solutions of the blue $Ni(P(CH_3)_3)_3Br_2$ complex are stable for longer periods than in other organic solvents and thus were chosen for detailed spectral study.

Electronic Spectrum of $Ni(P(CH_3)_3)_3Br_2$

The electronic spectrum of $Ni(P(CH_3)_3)_3Br_2$ in dichloromethane solution is given in Table I. The low-energy, ligand field bands are very similar to those of five-coordinate complexes known to be of approximately trigonal-bipyramidal structure.[14–20] Furthermore, the *relative* energies and intensities of the first two bands in $Ni(P(CH_3)_3)_3Br_2$ are very close to those of the complexes $Ni(P(C_6H_5)(OR)_2)_3(CN)_2$ (R = alkyl), which from infrared and electronic spectral studies have been shown to be close to *trans*-trigonal-bipyramidal structure.[19,20] Thus, we shall develop molecular orbital levels for a D_{3h} model *trans*-$Ni(PR_3)_3Br_2$ as the most convenient starting point in the discussion of the *observed* electronic energy levels of $Ni(P(CH_3)_3)_3Br_2$.

TABLE I

ELECTRONIC SPECTRUM OF $Ni(P(CH_3)_3)_3Br_2$ IN DICHLOROMETHANE SOLUTION AT 25°

Obsd max, cm^{-1} (ϵ)	$^1A_1' \rightarrow$
14,100 (600) 17,200 (800)	a^1E'
22,200 sh ($\sim$170)	a^1E''
26,200 (7000)	b^1E'
33,600 sh ($\sim$700)	b^1E''
36,400 sh ($\sim$3000)	c^1E'
40,400 (20,000)	$^1A_2''$

A molecular orbital energy level diagram for a model *trans*-$Ni(PR_3)_3Br_2$ system may be constructed by reference to the molecular orbital description derived previously for *trans*-$Ni(PR_3)_3(CN)_2$ systems.[19] The metal orbitals transform as follows: 3d(a_1', e′, e″); 4s(a_1'); 4p(a_2'', e′). The axial ligand σ orbitals transform as a_1' and a_2'', whereas the equatorial ones transform as e′ and a_1'; the Br $p\pi$ orbitals are e′ and e″. We have assumed the energy order $p\pi(Br) > \sigma(PR_3) > p\sigma(Br)$ in estimating the relative molecular orbital energies shown in Figure 1.

For an assumed *trans* structure, the ground state of $Ni(P(CH_3)_3)_3Br_2$ is $\ldots(2e'')^4(3e')^4 = {}^1A_1'$. The ligand field levels are $3a_1'$, 3e′, and 2e″. Two ligand field transitions are anticipated: $3e' \rightarrow 3a_1'$ ($^1A_1' \rightarrow a^1E'$) and $2e'' \rightarrow 3a_1'$($^1A_1' \rightarrow a^1E''$); the former is allowed, and the latter is forbidden. The bands observed at 14,100 and 17,200 cm^{-1} have moderate intensities and thus both must be *derived* from the allowed $^1A_1' \rightarrow a^1E'$ transition. This particular spectroscopic feature requires at least that the molecule be distorted from D_{3h} in the excited states derived from a^1E'; discussion of this point, however, is reserved until after the other bands are considered. The weak band at 22,200 cm^{-1} is assigned to the $^1A_1' \rightarrow a^1E''$ transition; the energy

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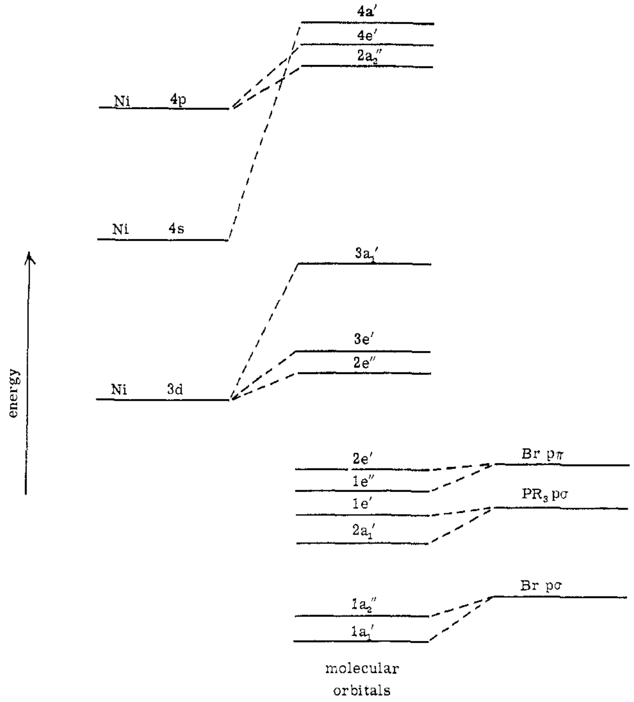

Figure 1.—Relative molecular orbital energies for *trans*-$Ni(PR_3)_3Br_2$ systems. Only the principal correlation lines are shown.

and intensity of this band are in good agreement with expectations.

There are three fully allowed charge-transfer transitions that should appear below 50,000 cm^{-1}. Thus the fact that three intense bands are observed is nicely compatible with the model. The assignments are as follows: 26,000 cm^{-1}, $2e' \rightarrow 3a_1'$ ($^1A_1' \rightarrow b^1E'$); 36,400 cm^{-1}, $1e' \rightarrow 3a_1'$ ($^1A_1' \rightarrow c^1E'$); and 40,400 cm^{-1}, $1a_2'' \rightarrow 3a_1'$ ($^1A_1' \rightarrow {}^1A_2''$).

The bands at 26,000 and 40,400 cm^{-1} are primarily $p\pi(Br) \rightarrow d\sigma^*$ and $p\sigma(Br) \rightarrow d\sigma^*$ transitions, respectively. Two bands attributable to these transitions are a well-established feature of square-planar MX_4^{n-} complexes (X = halide).[21] The band positions in the case of $Ni(P(CH_3)_3)_3Br_2$ are about as expected; for example, $AuBr_4^-$, which exhibits its lowest spin-allowed ligand field band at 18,520 cm^{-1}, has analogous charge-transfer bands at 24,810 and 39,680 cm^{-1}.[22]

A very interesting feature of the spectrum is the $\sigma[P(CH_3)_3] \rightarrow d\sigma^*$ band at 36,400 cm^{-1}. This transition energy should serve as a useful calibration point in discussions of charge-transfer spectra in four- and five-coordinate d^8 low-spin complexes containing phosphine and arsine ligands; because of the inherent simplicity of $P(CH_3)_3$, the assignment is less ambiguous here than in complexes containing more complicated phosphines.

The weak band at 33,600 cm^{-1} remains to be assigned. There is one orbitally forbidden $p\pi(Br) \rightarrow d\sigma^*$ charge-transfer transition which should appear in that region; the assignment suggested is $1e'' \rightarrow 3a_1'$ ($^1A_1' \rightarrow b^1E''$).

A summary of transition assignments for $Ni(P(CH_3)_3)_3Br_2$ is given in Table I. With the exception of the large splitting of the a^1E' state, the entire spectrum is consistent with the *trans* (D_{3h}) model. One reasonable interpretation of the spectroscopic results is that the ground state is indeed D_{3h} (or very nearly so) but the equilibrium internuclear configuration is closer to a tetragonal pyramid in the excited states derived from the $3e' \rightarrow 3a_1'$ transition. This suggestion is rather appealing because the configuration $\ldots(2e'')^4(3e')^3(3a_1')$ would be expected to profit from a distortion toward a tetragonal pyramid. In this connection, we recall that the d^7 system $Co(CN)_5^{3-}$ exhibits[23] a square-pyramidal ground-state structure (and the D_{3h} model in that case would also require three electrons in 3e'). Another possibility is that the ground state is not D_{3h} but rather is based on one of the idealized *cis* structures of an NiL_3X_2 trigonal bipyramid. Although this possibility is attractive insofar as the 14,100- and 17,200-cm^{-1} bands are concerned, we should expect a more complicated charge-transfer pattern than is observed. For this reason, we slightly favor the interpretation involving a D_{3h} ground state. Further discussion of structural matters, however, must await X-ray[24] and vibrational spectroscopic[20] studies now in progress on several complexes of the $Ni(P(CH_3)_3)_3X_2$ type.

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