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Five-Coordinate Cobalt(II) and Four- and Five-Coordinate Nickel(II) Complexes of the Flexible Triphosphine Ligand Bis(3-diphenylphosphinopropyl)phenylphosphine[1]

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Two series of low-spin cobalt(II) and nickel(II) complexes of the triphosphine ligand $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$ (ttp) *have been prepared and characterized. The electronic spectra of the complexes in the solid state (at 77°K and 300°K) and in solution (dichloromethane and acetonitrile) are used to assign coordination geometries and to determine the spectrochemical effect of the chelate chain length by comparison with the spectral data of corresponding complexes of* $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (etp). *The complexes M(ttp)X₂ (X = Cl, Br, I) are five-cordinate, square-pyramidal and the [Ni(ttp)X]PF₆ complexes are square planar. The nickel complexes form the five-coordinate cationic species* $[Ni(ttp)X(CH_3CN)]^+$ *in acetonitrile. The ligand* ttp *creates a lower spectrochemical effect than does the ligand* etp.

Introduction

The number of five-coordinate, low-spin nickel(II) and cobalt(II) complexes has recently increased so markedly that one might expect that the factors governing formation of a trigonal-bipyramidal, a square-pyramidal or an intermediate structure would be understood.[3] However, subtle changes in the nature of the connecting linkage between chelating donor groups, the types of donor atoms, the composition of the five ligands, and the d^n electron configuration can effect the ground state and/or the coordination geometry of the metal complex.[4]

To study the effect of the chelate chain length, we have examined nickel(II) and cobalt(II) coordination compounds of two closely related triphosphine ligands, *i.e.*, $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (*etp*)[5] and $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$ (*ttp*).[6] These two flexible ligands can be used to examine the electronic spectral and magnetic properties in complexes containing an equivalent P_3X_2 donor set. This paper reports the preparation and characterization of the $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$ complexes and compares the electronic spectra with selected complexes of $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$.

Experimental Section

All synthetic procedures were performed under a dry nitrogen atmosphere to minimize possible oxidation of the ligand.

Reagents. Acetonitrile and dichloromethane were purified by stirring 12 hrs over Linde molecular seives (4Å). Absolute ethanol and ethanol solutions of Ni^{II} and Co^{II} salts were degassed by refluxing under nitrogen. The ligand ttp, was prepared as described elsewhere[8] and was used as a benzene solution (4.1 ml/mmole). Metal salts and other reagents were obtained from commercial sources or prepared by standard methods.

Preparation of $M(ttp)X_2$ *complexes.* One millimole of $M(H_2O)_6X_2$ was dissolved in 30 ml of refluxing ethanol under nitrogen and 4.1 ml of the ligand solution (1 mmole) was added to the metal halide solution. The complexes crystallized rapidly from the solution; the mixtures were filtered, washed with ethanol and ether then dried on a sintered-glass frit under dry nitrogen. All complexes were recrystallized from dichloromethane-ethanol and dried *in vacuo* at 100° for 24 hrs. Yields of the recrystallized samples were *ca.* 70%.

$[Ni(ttp)X]PF_6$, *X = Cl, Br;* $[Ni_2(ttp)_2I_3]PF_6$. A dichloromethane solution of $Ni(ttp)X_2$ was stirred with a two fold excess of $NaPF_6$ for 30 min. and filtered.

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(2) This paper is based on part of the Ph.D. dissertation of T.E.N., The Ohio State University, 1972.

(3) Recent reviews on the five-coordinate complexes of Co^{II} and Ni^{II} include; L. Sacconi, «Transition Metal Chemistry», R.L. Carlin (Ed.), Dekker, New York *4*, 199 (1968); P.L. Orioli, *Coord. Chem. Revs.*, 6, 285 (1971); C. Furlani, *ibid.*, 3, 141 (1968); E.L. Mutterties and R.A. Schunn, *Quart. Revs.* (*London*), *20*, 245 (1966).

(4) L. Sacconi, *J. Chem. Soc.* (*A*), 248 (1970); L. Sacconi and R. Morassi, *ibid.*, 575 (1970).

(5) (a) J.C. Cloyd, Jr. and D.W. Meek, *Inorg. Chim. Acta*, 6, 607 (1972); (b) J. Terry, M.S. Thesis, The Ohio State University, 1971.

(6) The ligand $C_6H_3P[CH_2CH_2P(C_6H_5)_2]_2$ has previously been designated as DPP by us[5] and as Pf-Pf-Pf by King.[7] However, to provide a convenient comparison to the ligand $C_6H_5P[CH_2CH_2CH_2P(C_6H_3)_2]_2$, the abbreviations *etp* and *ttp* will be used in this paper for the triphosphine ligands containing ethylene and trimethylene connecting linkages, respectively.

(7) R.B. King, P.N. Kapoor, and R.N. Kapoor, *Inorg. Chem.*, *10*, 1841 (1971).

(8) T.E. Nappier, Jr. D.W. Meek, R.M. Kirchner, and J.A. Ibers, Accepted for publication in *J. Amer. Chem. Soc.*, *95*, *ca* August 1973

Table I. Characterization Data for the *ttp* Complexes.

Complex[a]		Λ_M[b] cm²/(ohm-mole)	μ_{eff}[c]	Elemental Analyses % C Calcd.	% C Found	% H Calcd.	% H Found	% Halide[d] Calcd.	% Halide[d] Found
Ni(ttp)Cl_2	Red-brown	*e*	0.36	62.44	61.89	5.39	5.23	10.25	10.40
Ni(ttp)Br_2	Brown	89	0.44	55.33	54.31	4.78	4.97	20.47	20.46
Ni(ttp)I_2	Deep red	113	0.37	49.38	48.97	4.26	4.16	29.01	28.91
[Ni(ttp)Cl]PF_6	Yellow	130	0.29	53.90	54.26	4.65	4.77	4.43	4.69
[Ni(ttp)Br]PF_6	Red-orange	124	0.28	51.07	49.79	4.41	4.42	9.45	14.61
					50.85		4.36		16.33
[Ni(ttp)I]PF_6	Red	124	0.41	48.38	48.19	4.18	4.36	14.21	13.98
[$Ni_2(ttp)_2I_3$]PF_6	Purple	124[f]	0.37	48.88	48.39	4.22	4.36	21.54	20.99
[Ni(ttp)NO_3]PF_6	Orange	241	0.34	52.17	51.94	4.50	4.47	1.69[g]	1.71
Co(ttp)Cl_2	Orange-brown	*e*	2.02	62.42	61.87	5.39	5.17	10.25	10.51
Co(ttp)Br_2	Brown	97	2.00	55.31	54.38	4.78	4.69	20.46	20.72
Co(ttp)I_2	Red-brown	128	2.01	49.37	49.01	4.26	4.08	29.01	29.30

[a] ttp is the ligand $C_6H_5P[CH_2CH_2CH_2P(C_6H_5)_2]_2$, $C_{36}H_{37}P_3$. [b] conductance in CH_3CN, 23°, *ca.* 0.001 *M;* typical uni-univalent electrolytes give values of 140-160 cm²/ohm-mole. [c] B.M., 23°, average of five different values of the magnetic field; corrected with the following Pascal constants: ttp, 385; Ni, 12; Co, 12; Cl, 25; Br, 35; I, 51; PF_6, 67; NO_3, 19. [d] halogen = the appropriate Cl, Br, or I. [e] not determined. [f] assuming 2[Ni(ttp)I]$^+$, I, PF_6; calculated per Ni ion. [g] % nitrogen.

An equal volume of ethanol was added to the filtrate; the volume of the solution was reduced by evaporating the dichloromethane until crystals began forming; the solution was cooled in a refrigerator and the resultant crystals were collected and recrystallized as described above. Yields were ~70%.

[Ni(ttp)I]PF_6; [Ni(ttp)(NO_3)]PF_6. An ethanol solution of "NiIPF_6" or "Ni(NO_3)PF_6" (1 mmole/30 ml) was prepared by metathesis of $Ni(NO_3)_2$ with the appropriate quantity of NaI and/or $NaPF_6$. The resultant solution was then treated as described for the M(ttp)X_2 preparation.

Spectral, Conductance, and Magnetic Measurements. These were obtained as described previously.[9] Solid state electronic spectra at 77°K were obtained as Nujol mulls immersed in liquid nitrogen in a quartz dewar.

Results and Discussion

Nickel(II) and cobalt(II) complexes of composition M(ttp)X_2 are formed and isolated readily from ethanol solutions of the MX_2 salts (Table I). These complexes are almost insoluble in ethanol, but they can be recrystallized easily from dichloromethane and ethanol without inclusion of solvent. Whereas the bromide and iodide complexes are quite soluble in dichloromethane, the corresponding chloride complexes are much less soluble; thus, they were purified by Soxhlet extraction. The solubility behavior of the *ttp* complexes was somewhat unexpected considering the high solubility of the Ni-*etp* complexes in ethanol and the difficulties encountered in obtaining crystals of the *etp* complexes.[5a]

Complexes of the formulation [Ni(ttp)X]PF_6 (where X = Cl, Br) are obtained easily when a solution of Ni(ttp)X_2 in dichloromethane is treated with a slurry of $NaPF_6$ (Table I). After removing the insoluble salts, the complexes are crystallized easily from ethanol. A similar procedure was followed in an attempt to prepare [Ni(ttp)I]PF_6; however, the analytical data for the purple crystals obtained from this reaction suggest the dimeric formulation [$Ni_2(ttp)_2I_3$]PF_6. Careful analysis of the infrared spectrum supports this suggestion; *e.g.*, the relative intensity of the phenyl-P-absorption *ca.* 1100 cm^{-1} compared with the PF_6^- band at 558 cm^{-1} (ν_4, T_{1u})[10] in this complex is much stronger than for [Ni(ttp)X]PF_6 (X = Br, Cl) complexes . Electronic spectra to be discussed later also support the dimeric formulation. However, the anticipated complex [Ni(ttp)I]PF_6, was prepared from an ethanol solution of "NiIPF_6" which had been prepared *in situ* from $Ni(NO_3)_2$. The complex [Ni(ttp)-(NO_3)]PF_6 was prepared similarly. Infrared bands attributable to coordinated NO_3^- occur at 1490vs, 1278vs, 1272vs, 979s, 789m,sp,[11] and 714w,sp cm^{-1}.[11] While no distinction between mono- and bidentate NO_3^- can be made with certainty from infrared data alone,[12] the electronic spectrum provides evidence for monodentate NO_3^-.

Attempts to prepare the four-coordinate complexes [Co(ttp)X]PF_6 by simple metathesis of Co(ttp)X_2 compounds resulted in decomposition of the sample. Usually intractable blue solids were obtained; a similar behavior has been observed previously[5b,7] with cobalt(II) complexes of *etp.*

Conductivity measurements in acetonitrile are consistent with uni-univalent electrolytes for all complexes except the M(ttp)Cl_2 complexes which are too insoluble for accurate conductivity measurements and the nitrate complex which is a di-univalent electrolyte. The soluble M(ttp)X_2 complexes show variable degrees of halide dissociation; *e.g.* the values range up to 128 cm²/(ohm-mole) for Co(ttp)I_2, indicative of nearly complete dissociation into a uni-univalent electrolyte.

The Co(ttp)X_2 complexes are paramagnetic (μ_{eff} = ~2.01 B.M.), consistent with one unpaired electron

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

[10] G.M. Begun and A.C. Rutenberg, *ibid.*, *6*, 2212 (1967).

[11] These peaks are assigned tentatively to the NO_3^- group, as the triphosphine ligand also has absorption peaks in these regions; vs, s, and m = very strong, strong, and medium intensity, respectively; sp = sharp.

[12] N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, *4*, 804 (1965).

Table II. Electronic Spectral Data for the Cobalt(II) and Nickel(II) Complexes, kK.

	Solid State (Nujol mulls)		Solution	
	(~298° K)	77°K	CH_2Cl_2	CH_3CN
$Ni(ttp)Cl_2$	16.7sh	16.6	16.9sh(226)	
	22.5	21.8	22.2(1276)	
		23.1	30.3(12100)	
			37.6(15200)	
$Ni(ttp)Br_2$	16.4sh	16.1	16.4sh(217)	21.8(1630)
	21.6	21.2	21.4(1258)	32.8(13500)
		21.8sh	31.6(13500)	37.6(15400)
			38.0(18800)	
$Ni(ttp)I_2$	15.6sh	16.1sh	14.9sh(230)	21.1(1552)
	19.5	19.9	19.5(1313)	31.9(17700)
		25.3sh	30.8(18400)	36.6(13500)
			36.2(19500)	
$Ni(ttp)Cl^+$	23.5	23.9	23.2(1474)	22.6(1476)
	29.6	30.1	30.0(12800)	30.6(13200)
	33.1sh		35.2(17200)	37.9(15900)
	35.7			
$Ni(ttp)Br^+$	21.6	21.9	22.3(1171)	22.0(1714)
	29.2	29.6	30.1sh(8710)	30.9(13000)
		32.8sh	31.6(9560)	32.8(13200)
			37.9(18700)	37.3(13800)
$Ni(ttp)I^+$	22.2	20.8sh	20.5(874)	17.5sh(458)
	30.9	22.9	31.3sh(11800)	21.1(1570)
			35.5(>20000)	32.1(18000)
				36.6(13600)
$Ni_2(ttp)_2I_3^+$	19.4	17.7sh	15.2sh(150)	21.2(1660)
	27.6	19.9	19.8(1062)	32.1(18900)
			30.8(14600)	36.8(14200)
			35.5(19300)	
$Ni(ttp)NO_3^+$	24.0	24.4	23.6(2000)	23.5(1960)
	29.2	29.8	29.2(15300)	30.0(16600)
			36.5(19800)	
$Co(ttp)Cl_2$	7.46	7.46	7.49(36)	
	14.5sh	14.3	14.3sh(86)	
	18.2sh	18.3	17.9sh(327)	
	22.3	23.1	22.3(1178)	
			29.9(6900)	
$Co(ttp)Br_2$	7.58	7.52	7.46(37)	6.67(96)
	13.9sh	13.9	13.9sh(78)	23.4(1554)
	17.9sh	17.9	17.2sh(319)	25.8(2060)
	22.1	22.9	21.7(1191)	32.3(8980)
		26.7sh	29.4sh(4140)	
$Co(ttp)I_2$	7.25	7.46	6.90(38)	6.58(119)
	12.7	12.7	12.8(77)	19.2sh(323)
	16.8	16.9	15.9(332)	23.6(2830)
	21.4	21.2	21.1(1640)	32.7(13900)
		21.9	27.0sh(2620)	
		24.3	35.7sh(15200)	

with some orbital contribution. This value is within the range of 2.0-2.3 B.M. found in other low-spin, five-coordinate Co^{II} complexes.[13] The Ni^{II}-ttp complexes are all diamagnetic, exhibiting only a small temperature independent paramagnetism (0.3-0.4 B.M.).

Nickel(II) Electronic Spectra. Spectral data for the Ni^{II} and Co^{II} complexes are presented in Table II and some selected spectra are plotted in Figures 1-4. The electronic spectra of the $Ni(ttp)X_2$ complexes are quite similar to those observed for square-pyramidal complexes of C_s microsymmetry, *e.g.* the number of bands, their energy values and their relative intensities compare favorably with those of $Ni(DAP)(CN)_2$[14] (DAP = $C_6H_5P[CH_2CH_2CH_2As(CH_3)_2]_2$) and $[Ni(TEP)_2I]I$[15] (TEP = $(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$), whose structures have been determined by X-ray crystallography. Consequently, the electronic spectra of the nickel complexes are interpreted on the basis of square-pyra-

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(13) G. Dyer and D.W. Meek, *J. Amer. Chem. Soc.*, *89*, 3983 (1967); M.J. Norget, J.H.M. Thornley, and L.M. Venanzi, *J. Chem. Soc.* (*A*), 540 (1967).

(14) C.A. McAuliffe, M.O. Workman, and D.W. Meek, *J. Coord. Chem.*, *2*, 137 (1972).

(15) E.C. Alyea and D.W. Meek, *Inorg. Chem.*, *11*, 1029 (1972). (1970).

(16) J.R. Preer and H.B. Gray, *J. Amer. Chem. Soc.*, *92*, 7306

midal Ni(ttp)X_2 and square-planar $[Ni(ttp)X]^+$ complexes. Using the arrangement of d-orbital energy levels suggested by Preer an dGray,[16] the energy level diagrams for C_{2v} and C_s symmetries (X as primary axis) can be constructed (Figure 5).

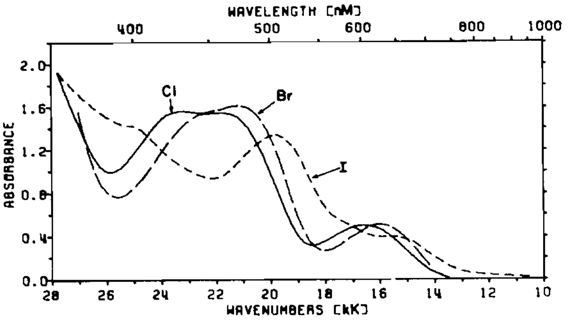

Figure 1. Electronic spectra of solid Ni(ttp)X_2 complexes at 77°K: X = Cl, ——; Br, — — —; I, - - - -.

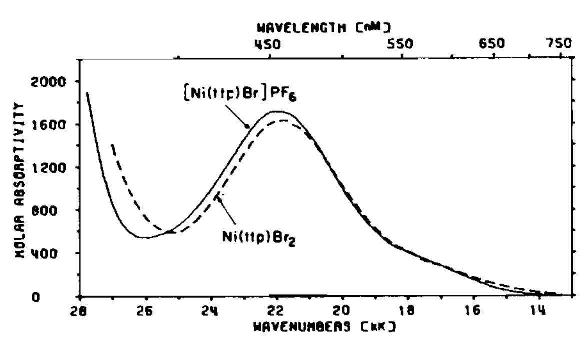

Figure 2. Electronic spectra of $[Ni(ttp)Br]PF_6$ (——) and Ni(ttp)Br_2 (- - - -) in acetonitrile solutions.

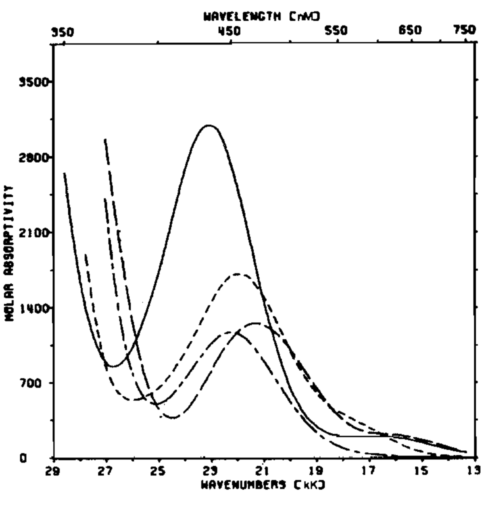

Figure 3. Electronic spectra of solutions of Ni(etp)Br_2 in 1,2-dichloroethane (——), $[Ni(ttp)Br]PF_6$ in acetonitrile (- - - -), $[Ni(ttp)Br]PF_6$ in dichloromethane (— - — -), and Ni(ttp)Br_2 in dichloromethane (— — —).

The visible spectra of the Ni(ttp)X_2 complexes in the solid state and dichloromethane solution exhibit two main bands, one at low energy (~16 kK, ε ~200) and one at high energy (~21 kK, ε ~1300). The former is assigned to the$^1A' \rightarrow {}^1A'$ ($d_{z^2} \rightarrow d_{x^2-y^2}$) transition, while the latter is attributed to the ($d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$) electronic transition. The most unusual feature of the Ni(ttp)X_2 (X = Cl, Br) spectra is the splitting of the band at ~21-23 kK observed at 77°K (Figure 1). This is consistent with the proposed energy levels in Figure 5 where the d_{xz} and d_{yz} orbitals are closely spaced but non-degenerate.

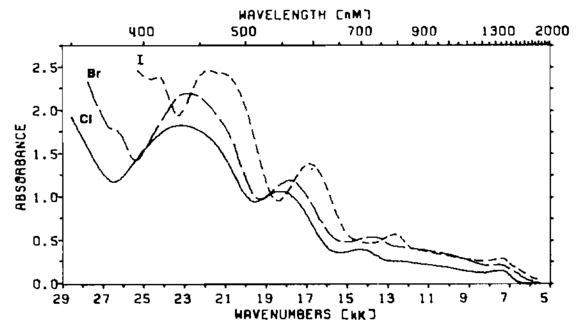

Figure 4. Electronic spectra of Co(ttp)X_2 complexes at 77°K: X = Cl, ——; Br, — — —; I, - - - -.

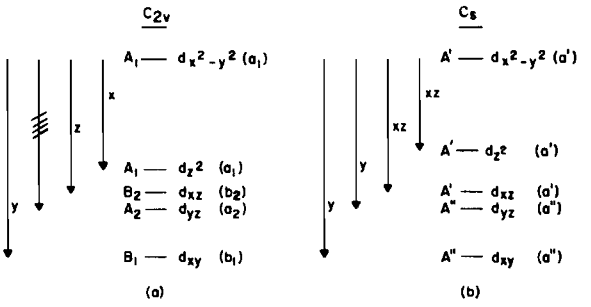

Figure 5. d-Orbital energy levels, with appropriate labels, for the C_{2v} and C_s microsymmetries of the four-coordinate $[M(ttp)X]^+$ (a) and five-coordinate M(ttp)X_2 complexes (b). The arrows are drawn on the basis of the "hale" formalism.

The electronic spectra of the Ni(ttp)X_2 complexes in acetonitrile (Figure 2; Table II) show a broad band on the low energy side of the intense band, indicating a five-coordinate species—either through coordination of acetonitrile or incomplete halide dissociation. The former explanation is preferred on the basis of the conductance measurements, particularly for Ni(ttp)I_2 (Λ_M = 113 cm^2/(ohm mole), Table I). Solvation also is indicated by the spectra of the $[Ni(ttp)X]PF_5$ complexes, which are remarkably similar to the spectra of the corresponding Ni(ttp)X_2 complexes in acetonitrile (Figure 2). A further indication that the $[Ni(ttp)X]PF_5$ complexes become five-coordinate in acetonitrile can be seen by comparing the spectrum of $[Ni(ttp)Br]^+$ with that of the same complex in dichloromethane (Figure 3). In dichloromethane the $[Ni(ttp)Br]^+$ complex has a lower molar absorptivity and does not display the lower energy shoulder at ~18 kK that is observed acetonitrile solutions. The spectra of $[Ni(ttp)X]PF_6$ in dichloromethane and in the solid state are explained in terms of a four-coordinate, square-planar complex with C_{2v} microsymmetry. The strong band is assigned as the allowed transition $^1A_1 \rightarrow {}^1B_2$-($d_{xz} \rightarrow d_{x^2-y^2}$); the $^1A_1 \rightarrow {}^1A_1$ ($d_{z^2} \rightarrow d_{x^2-y^2}$) transition is possibly buried under the strong $^1A_1 \rightarrow {}^1B_2$ absorption.

The visible spectrum of $[Ni(ttp)(NO_3)]PF_6$ in the solid state and in dichloromethane solution shows a similar single strong band which indicates that the complex is four-cordinate; thus the NO_3^- is acting as a monodentate ligand. The spectrum is virtually identical in acetonitrile (Table II), but the molar conductance signifies a di-univalent electrolyte in this solvent. This suggests that $[Ni(ttp)(CH_3CN)]^{2+}$ is formed in acetonitrile.

The spectra of the cationic nickel iodide complexes are complicated by the apparent presence of bridging iodide. The solid state spectra of $Ni(ttp)I_2$, $[Ni(ttp)I]PF_6$, and $[Ni(ttp)_2I_3]PF_6$ (Table II) are all similar, exhibiting a shoulder on the low energy side of the intense main band which suggests five-coordinate nickel(II).

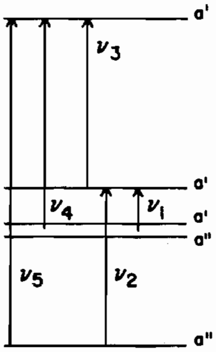

Figure 6. Assignment of the electronic transitions on a qualitative d-orbital energy level diagram for the five-coordinate $Co(ttp)X_2$ complexes.

Cobalt(II) Electronic Spectra. The analogous stoichiometry and electronic spectral similarities (Table II and Figure 4) suggest that the $Co(ttp)X_2$ complexes also posses a square-pyramidal structure. Using the same energy level diagram (Figure 5b) and C_s microsymmetry as for the square-pyramidal nickel(II) complexes, the observed transitions can be assigned as in Figure 6, where the energy range (kK) from iodide to chloride is:

$\nu_1 = 6.90 - 7.49 \quad \varepsilon \sim 30$

$\nu_2 = 12.8 - 14.3 \quad \varepsilon \sim 80$

$\nu_3 = 15.9 - 17.9 \quad \varepsilon \sim 300$

$\nu_4 = 21.1 - 22.3 \quad \varepsilon \sim 1200$

$\nu_5 = 27.0 - 29.9 \quad \varepsilon \sim 4000$

The assignment of ν_5 as a *d-d* transition is questionable[17] since charge transfer bands also begin to appear at these energies.

This order of d-orbital energies for square-pyramidal Co^{II} is supported by the theoretical treatment[18] of $[Co(CN)_5]^{3-}$ and by a comparison of the position of ν_3 and ν_4 with the $Ni(ttp)X_2$ complexes. Also, the intensities and number of peaks observed in the electronic spectra of the $Co(tpp)X_2$ complexes correspond closely to those of the known square-pyramidal complex $[Co(diphos)_2Cl]SnCl_3$ (where diphos = Ph_2P $CH_2CH_2PPh_2$).[19]

Spectral Effect of Five- and Six-membered Chelate Rings. Both ligands *etp* and *ttp* give low-spin nickel (II) complexes of composition $Ni(ligand)X_2$. The electronic spectra of the $Ni(ligand)X_2$ complexes taken in Nujol mulls at 77°K and 300°K, and in dichloromethane solution at 300°K show two ligand field bands in the visible region. These spectra are characteristic of low-spin, five-coordinate Ni^{II} complexes with coordination geometries intermediate between the idealized trigonal-bipyramidal and square-pyramidal structures, but more closely approximating the latter. Both series of complexes are approximately uni-univalent electrolytes in acetonitrile, and the implied existence of the cations, $[Ni(ligand)X]^+$, is confirmed by the isolation of the four-coordinate complexes $[Ni(etp)X]B(C_6H_5)_4$ and $[Ni(ttp)X]PF_6$. The visible electronic absorption spectra of the corresponding complexes $[Ni(ligand)X]^+$ and $Ni(ligand)X_2$ in acetonitrile solutions are quite similar. The $[Ni(ttp)X]^+$ complexes tend to form a five-coordinate species in acetonitrile solution more than the corresponding $[Ni(etp)X]^+$ complexes; this is concluded from the absence of the lower energy band in the electronic spectra of the $[Ni(etp)X]^+$ complexes.

Ligand field effects are observed not only in the band positions, but also in the molar absorptivities. The main electronic spectral maxima of the complexes $Ni(ttp)X_2$ and $[Ni(ttp)X]^+$ are displaced consistently ($\sim$2,000 cm^{-1}) to lower energies as compared to the corresponding complexes of *etp* (Table II and Figure 3).[5a] Similarly the molar absorptivities of this band for the *ttp* complexes are $\sim$50% lower than for the corresponding *etp* complexes. These observations can be interpreted as being due to a tighter fit of the *etp* ligand on nickel which causes the phosphorus atoms to be located at positions significantly removed from those of an ideal square pyramid.[20] This chelation compression effect (particularly at the central phosphorus atom) is apparently greater than the stabilization expected in the case of *ttp* as a result of more ideal Ni-P bond distances and angles in the basal plane of the square pyramid.

Although equilibrium constants have not been determined, it appears that the six-membered rings of *ttp* facilitate formation of five-coordinate nickel(II)

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[17] A referee has questioned assignment of bands at 27 kK and $\varepsilon \sim 4000$ as a d-d transition. These bands appear as shoulders (Br, I) or a slight peak (Cl) on the side of a much more intense band ($\varepsilon \sim 15,000$). We estimate that Gaussian analysis of these spectra would *reduce the reported molar absorptivity by at least 50%.*

[18] A.O. Caride, H. Panepucci, and S.I. Zanette, *J. Chem. Phys.*, *55*, 3651 (1971).

[19] J.K. Stalick, G. Dyer, C.A. McAuliffe, and D.W. Meek, to be submitted soon for publication; see structural details in J.K. Stalich, P.W.K. Carfield, and D.W. Meek, *Inorg. Chem.*, *12*, June 1973.

[20] After this paper was submitted, an X-ray structural determination of $Ni(etp)(NCS)_2$ [J. Stalick and D.W. Meek, unpublished data, 1972] showed that the inner coordination geometry is approximately a square pyramid with the tridentate ligand in the basal plane. The *chelate ring is considerably strained as the Ni-P bond distance to the* central phosphorus atom is 0.09 Å shorter than the distances to the two terminal phosphorus atoms and the P_{term}-Ni-P_{term} angle is $\sim$160° *rather than the more ideal 180°.*

complexes more readily than the same set of donor atoms with five-membered chelate rings; however, the ligand field effect of the six-membered ring is lower than for the analogous five-member ring.

Similar comparisons can be made for the cobalt(II) complexes, and generally the same trends are observed. However, these comparison are complicated by the oxygen sensitivity of the Co(etp)X_2 complexes and by their tendency to undergo isomerization to a tetrahedral complex, particularly in solution.

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