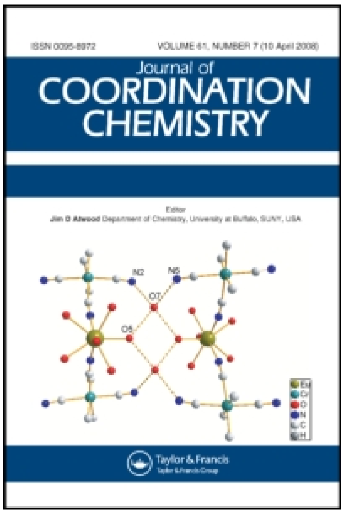


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

TRI (2-PYRIDYL) PHOSPHINE, TRI(2-PYRIDYL) PHOSPHINE OXIDE, AND TRI (2-PYRIDYL) ARSINE METAL (II) PERCHLORATE COMPLEXES

Robert K. Boggess[a][b]; David A. Zatko[a]
[a] Department of Chemistry, The University of Alabama, University, Alabama, USA [b] Thomas More College, Covington, KY

To cite this Article Boggess, Robert K. and Zatko, David A.(1975) 'TRI (2-PYRIDYL) PHOSPHINE, TRI(2-PYRIDYL) PHOSPHINE OXIDE, AND TRI (2-PYRIDYL) ARSINE METAL (II) PERCHLORATE COMPLEXES', Journal of Coordination Chemistry, 4: 4, 217 — 224

To link to this Article: DOI: 10.1080/00958977508075903

URL: http://dx.doi.org/10.1080/00958977508075903

J. Coord. Chem.
1975, Vol. 4, pp. 217–224

TRI (2-PYRIDYL) PHOSPHINE, TRI(2-PYRIDYL) PHOSPHINE OXIDE, AND TRI (2-PYRIDYL) ARSINE METAL (II) PERCHLORATE COMPLEXES[1]

ROBERT K. BOGGESS[2] and DAVID A. ZATKO

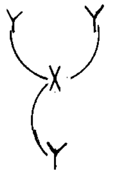
Department of Chemistry, The University of Alabama, University, Alabama 35486, USA

(*Received February 19, 1973, in final form August 26, 1974*)

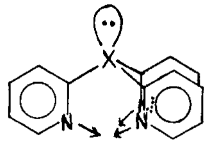
Metal(II) perchlorate complexes with the ligands tri(2-pyridyl)phosphine, tri(2-pyridyl)phosphine oxide, and tri(2-pyridyl)arsine have the composition $[M(TPX)_2](ClO_4)_2$. Coordination occurs only through the nitrogens of the pyridines. In the case of Cu(II) and tri(2-pyridyl)phosphine oxide, two isomers were obtained. One isomer contains symmetrical tridentate tri(2-pyridyl)phosphine oxide ligands while the second isomer contains an unsymmetrical ligand. The unsymmetrical tri(2-pyridyl)phosphine oxide may be a bidentate ligand or a bridging tridentate. Weak axial interaction between a pyridyl group and a second Cu(II) ion is postulated in solution and may be present in the solid state.

INTRODUCTION

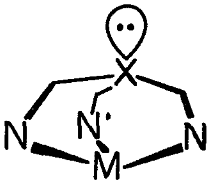
Ligands which contain three donor atoms(Y) connected to a fourth potential donor(X) through various types of linkages(I) are well known.[3] When the "chains" connecting the X-donor atom to the Y-donor atoms are sufficiently flexible, all four atoms can coordinate. In such cases, the ligands can impose a trigonal-bipyramidal or square pyramidal coordination around the metal ion.[3] The more inflexible ligands have not been well studied. McWhinnie, *et al.* have studied several complexes with tri(2-pyridyl)amine[4-9] (TPAm, II with X = N) where the chain connecting the two types of donor atoms is an α-carbon of a pyridine ring. This one-atom chain directs the lone-pair of electrons on the amine nitrogen atom away from the pyridyl nitrogen lone pair of electrons and only coordination through the pyridyl nitrogens has been observed for TPAm. However, coordination is not restricted to tridentate chelation as both bidentate and tridentate chelation (modes III and IV below) have been found. Other modes of coordination (V, VI, and VII below) which involve the central atom have not been found for TPAm. The larger covalent radius of a phosphorus or arsenic central atom [the covalent radii increase in the series N(0.75 A), P(1.10 A), As(1.21 A)[10,11]] may promote geometric rearrangements in ligand coordination.



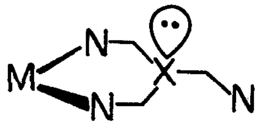
I



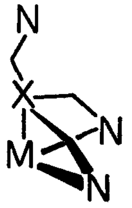
II



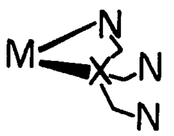
III



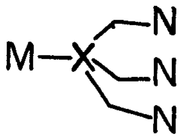
IV



V



VI



VII

In order to determine if the central atom in II can markedly influence the mode of coordination to a given metal, we have prepared and characterized the first row transition metal(II) perchlorate complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with tri(2-pyridyl)phosphine (TPP, II with X = P), tri(2-pyridyl)phosphine oxide (TPPO, II with X = P(O)), and tri(2-pyridyl)arsine (TPAs, II with X = As).

EXPERIMENTAL SECTION

Reagents

Reagents, with their source given in parentheses, are listed below: hydrated metal perchlorates (G. F. Smith Chemical Co., Columbus, Ohio); n-butyllithium in n-hexane (Foote Mineral Company, Exton, Pa.); 2-bromopyridine (Reilly Tar and Chemical Co., Indianapolis, Ind.); trichlorophosphine and trichloroarsine (Alfa Inorganics, Beverly, Mass,); nitromethane, acetonitrile, 2,2-dimethoxypropane, triethyl orthoformate (Aldrich Chemical Co., Milwaukee, Wis.); and anhydrous ether (Mallinckrodt Chemical Works, St. Louis, Mo.).

Syntheses

Tri(2-pyridyl)phosphine was prepared by a modified method of Plazek and Tyka.[12] 2-Bromopyridine (66.8 ml, 0.70 mole) in 250 ml of anhydrous ether was added with stirring and under a nitrogen atmosphere to a solution of n-butyllithium (1.6M in n-hexane, 0.70 mole) in three pounds of anhydrous ether after cooling both solutions to –65°C. The dark-red solution was stirred for 15 minutes before adding trichlorophosphine (18.3 ml, 0.21 mole) in 100 ml of anhydrous ether. The reaction mixture was kept at –65°C under nitrogen for an additional 15 minutes, then allowed to warm to room temperature. The product was extracted from the ether layer by the slow addition of 300 ml of 3.6M H_2SO_4 while the reaction mixture was cooled in an ice-water bath and nitrogen passed over the solution. The ether layer was discarded and the product was precipitated by the slow addition of NaOH solution (100 g/200 ml of H_2O) with the solution again cooled in an ice-water bath and kept under a nitrogen atmosphere. The precipitate was filtered and washed with water to rid it of Na_2SO_4. A pure product was obtained by two recrystallizations from a 1:1(v/v) mixture of methanol and water. Yields ranged from 30 to 40%; m.p. 110.5°C, uncorrected (lit. value 115°C).[13] The remaining methanol-H_2O filtrate contained both TPP and its phosphine oxide (TPPO). This was converted solely to TPPO by the addition of 30% H_2O_2 (5 ml). Recrystallization from 95% ethanol gave a pure product; m.p. 216–217°C, uncorrected (lit. value 209°C).[13]

Tri(2-pyridyl)arsine was prepared in the same manner as TPP, except that trichloroarsine (17.6 ml,

TABLE I

Elemental analyses for the M(TPX)$_2$(ClO$_4$)$_2$ complexes

	%C		%H		%N	
	Theory	Found	Theory	Found	Theory	Found
Mn(TPP)$_2$(ClO$_4$)$_2$	45.94	45.53	3.08	3.12	10.71	11.00
Co(TPP)$_2$(ClO$_4$)$_2$	45.71	45.37	3.07	3.05	10.66	10.80
Ni(TPP)$_2$(ClO$_4$)$_2$	45.72	45.76	3.07	2.93	10.66	10.49
Cu(TPP)$_2$(ClO$_4$)$_2$	45.44	45.78	3.05	3.08	10.60	10.70
Zn(TPP)$_2$(ClO$_4$)$_2$	45.34	45.47	3.04	2.97	10.57	10.50
Mn(TPPO)$_2$(ClO$_4$)$_2$	44.15	44.18	2.96	3.03	10.29	10.30
Co(TPPO)$_2$(ClO$_4$)$_2$	43.92	44.05	2.95	2.97	10.24	10.37
Ni(TPPO)$_2$(ClO$_4$)$_2$	43.94	44.00	2.95	2.97	10.25	10.13
Cu(TPPO)$_2$(ClO$_4$)$_2$-green	43.68	43.56	2.93	2.98	10.19	10.09
Cu(TPPO)$_2$(ClO$_4$)$_2$-blue	43.68	43.55	2.93	2.98	10.19	10.24
Zn(TPPO)$_2$(ClO$_4$)$_2$	43.58	43.34	2.93	2.96	10.16	10.20
Mn(TPAs)$_2$(ClO$_4$)$_2$	41.31	41.48	2.77	2.87	9.63	9.64
Co(TPAs)$_2$(ClO$_4$)$_2$	41.12	41.12	2.76	2.75	9.59	9.63
Ni(TPAs)$_2$(ClO$_4$)$_2$	41.13	41.16	2.76	2.86	9.59	9.62
Cu(TPAs)$_2$(ClO$_4$)$_2$	40.91	40.90	2.75	2.89	9.54	9.50
Zn(TPAs)$_2$(ClO$_4$)$_2$	40.82	40.91	2.74	2.75	9.52	9.41

0.21 mole) was added to the 2-lithiopyridine. After extraction with H_2SO_4 and precipitation with NaOH, the oily material was dissolved in a 1:1(v/v) mixture of methanol and water and stirred with activated charcoal. The charcoal was filtered off after 15 minutes, and the solvent was removed by a rotary evaporator. The still impure product was placed in 500 ml of n-hexane and the mixture heated to boiling. After an intractable oil formed at the bottom of the beaker, the hot solution was quickly poured off and a pure product precipitated upon cooling. Extraction of pure product from this oily residue was repeated until no more product precipitated from the n-hexane. Yields ranged from 40 to 50%; m.p. 82–83°C, uncorrected (lit. value 85–85.5°C).[13]

In a typical preparation of the complexes, the $[M(H_2O)_6](ClO_4)_2$ (0.005 mole) was refluxed for 1 to 12 hours in 95% ethanol (50 ml) and 2,2-dimethoxypropane (50 ml) under a nitrogen atmosphere before adding the ligand (0.010 mole) dissolved in 95% ethanol. Precipitation occurred in a few minutes. The reaction mixture was heated under nitrogen for 1 to 2 hours and then cooled. The solid was collected on a medium porosity frit and washed with 95% ethanol. Heating in 95% ethanol (25 ml) and 2,2-dimethoxypropane (25 ml) under nitrogen was repeated before the precipitate was collected and dried at 90 to 100°C *in vacuo*. Yields were greater than 80%.

In one preparation $[Cu(H_2O)_6](ClO_4)_2$ was heated in 95% ethanol and 2,2-dimethoxypropane. The solution turned deep-red, indicating some decomposition of the solvent system. When the ligand TPPO was added, a blue complex was obtained. With triethylorthoformate as the dehydrating agent, a light green complex was obtained with TPPO.

Physical Measurements

Resistance measurements at 25.0 ± 0.1°C were taken in a Fisher Scientific Products Company cell ($k = 1.45\ cm^{-1}$) with heavily platinized platinum electrodes with a Beckman Instruments, Inc., Model RC-18 conductivity bridge (1 kHz). Conductivity titrations were performed at room temperature in an electrolytic beaker using a conventional dip-type platinum electrode and an Industrial Instruments, Inc. Model RC-16B2 conductivity bridge (60 Hz).

Infrared spectra were taken as mineral oil or hexachlorobutadiene mulls with a Perkin-Elmer 337 grating spectrophotometer. All spectra were calibrated with polystyrene at 1601 cm^{-1} and 906 cm^{-1}.

Electronic absorption spectra of solutions were obtained with a Cary Model 14 recording spectrophotometer using matched 10.00 cm quartz cells.

Analyses

Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga., and PCR, Inc., Gainesville, Fla.

RESULTS AND DISCUSSION

When TPP, TPPO, and TPAs react with metal(II) perchlorates, complexes of the composition $[M(TPX)_2](ClO_4)_2$, where M = Mn, Co, Ni, Cu, and Zn and TPX = TPP, TPPO, and TPAs, are obtained (Table 1). Each complex in a given series, e.g., $[Mn(TPP)_2](ClO_4)_2$, $[Mn(TPPO)_2](ClO_4)_2$, and $[Mn(TPAs)_2](ClO_4)_2$, has the same color indicating that the ligand field splittings of the ligands are approximately equal. This result initially suggests that all the ligands coordinate similarly and that the central atom has a negligible effect upon the electronic structure of the metal ion.

The ligands are basically 2-substituted pyridines and extensive infrared correlations have been made for these compounds.[14] The four pyridine skeletal bands observed between 1600 and 1420 cm^{-1} and the ClO_4^- bands at 1100 cm^{-1} (ν_3) and 625 cm^{-1} (ν_4) are the vibrations of interest in determining coordination to a metal. Other pyridyl bands such as the ring-breathing mode near 1000 cm^{-1}, the out-of-plane CH deformation near 800 cm^{-1}, and the skeletal mode near 740 cm^{-1} have previously been used in deducing the structure of pyridine complexes,[15] but of these only the bands near 1000 cm^{-1} have been tabulated (Table II).

All of the complexes, except $[Cu(TPPO)_2](ClO_4)_2$-blue, exhibit four $\nu_{(C=C)}$, $\nu_{(C=N)}$ skeletal vibrations in the following ranges: band I, 1575–1590 cm^{-1}; band II, 1550–1565 cm^{-1}; band III, 1445–1460 cm^{-1}; and IV, 1425–1430 cm^{-1}. The presence of only four bands indicates that all the pyridyl rings are nearly equivalent.[14] Band I in all the complexes is increased from its free ligand position and the ring-breathing mode of the free ligand at 990 cm^{-1} has been increased to between 1000 and 1022 cm^{-1} in the complexes; both of these increases have been taken to indicate pyridine coordination.[16,17] The ν_3 and ν_4 bands of the ClO_4^- group exhibit no splitting, thus indicating that they are ionic and non-coordinated.[18] Overall, the infrared data suggests that the complexes can be formulated as $[M(TPX)_2](ClO_4)_2$ with symmetrical tridentate ligands (mode III) and ionic ClO_4^- in the solid state.

An interesting feature of the infrared spectra of the $[M(TPPO)_2](ClO_4)_2$ complexes is the increase in frequency of the P=O stretch from that of the free ligand. When phosphine oxides complex through the oxygen atom there is a decrease in the frequency of the P=O.[19] This has been interpreted as a decrease in the bond order of the P=O group by promoting a large ionic contribution of the form $P^+{-}\bar{O} \rightarrow M$. Consequently, the shifts to higher frequency observed for the TPPO complexes cannot arise from oxygen coordination to other metal ions, but must arise from the configuration imposed upon the ligand by coordination and the resulting electronic rearrangements, or by the mass effect of the large metal ion on the vibrations of the ligand. Bell, *et al.*,[20] have shown that the P=O frequency for tri-substituted phosphine oxides is determined mainly by the electrical effect of the substituent upon the force constant rather than by a mass effect. Thus, the infrared data indicate that there is less charge separation in the P=O group after complexation. Coordination of the positive metal ion has apparently increased the electronegativity of the pyridyl ring and consequently imparted a higher electronegativity to the phosphorus atom. This lessens the contribution of the $P^+{-}O^-$ form and increases the P=O frequency.

Conductivity titrations of the metal(II) perchlorates with TPP and TPAs in nitromethane clearly show the formation of the bis complexes and the initial formation of a mono complex for several of the metals (Figure 1). Single-concentration conduc-

TABLE II
Selected infrared data for TPX and the $M(TPX)_2(ClO_4)_2$ complexes[a,b]

	Pyridyl	Perchlorate	Other
TPP	1550(s), 1415(s), 1405(s)		989(s), 984(s)
$Mn(TPP)_2(ClO_4)_2$	1575(s), 1550(sh), 1425(s)	1110–1080(vs), 617(s)	1008(m)
$Co(TPP)_2(ClO_4)_2$	1580(s), 1550(sh), 1425(s)	1100–1070(vs), 617(s)	1012(m)
$Ni(TPP)_2(ClO_4)_2$	1580(s), 1555(sh), 1430(s)	1100–1070(vs), 616(s)	1014(m)
$Cu(TPP)_2(ClO_4)_2$	1580(s), 1555(sh), 1425(s)	1100–1080(vs), 617(s)	1017(w), 1005(w)
$Zn(TPP)_2(ClO_4)_2$	1575(s), 1557(sh), 1430(s)	1100–1080(vs), 615(s)	1010(m)
TPPO	1565(s), 1555(sh), 1420(s)		1215(s), 992(s)
$Mn(TPPO)_2(ClO_4)_2$	1580(s), 1565(sh), 1450(m)*, 1420(s)*	1095–1075(vs), 615(s)	1231(s), 1008(m)
$Co(TPPO)_2(ClO_4)_2$	1575(s), 1550(sh), 1450(m)*, 1430(s)*	1100–1075(vs), 614(s)	1236(s), 1010(m), 1003(sh), 988(m)
$Ni(TPPO)_2(ClO_4)_2$	1590(s), 1555(sh), 1445(sh)*, 1425(s)*	1095–1075(vs), 612(s)	1236(s), 1010(m), 1000(sh), 985(m)
$Cu(TPPO)_2(ClO_4)_2$-green	1575(s), 1550(sh), 1450(m)*, 1420(s)*	1100–1080(vs), 619(s)	1236(s), 1022(m), 1002(m)
$Cu(TPPO)_2(ClO_4)_2$-blue	1600(sh), 1580(s), 1560(sh), 1500(m)*, 1480(s)*, 1460(sh)*, 1450(s)*, 1440(s)*	1090–1070(vs), 615(s)	1235(s), 1018(w), 1000(w)
$Zn(TPPO)_2(ClO_4)_2$	1580(s), 1560(sh), 1450(m)*, 1425(s)*	1100–1080(vs), 613(s)	1232(s), 1010(m)
TPAs	1555(s), 1444(s), 1417(s)		988(s)
$Mn(TPAs)_2(ClO_4)_2$	1575(s), 1550(sh), 1455(s)*, 1420(s)*	1100–1080(vs), 615(s)	1010(m)
$Co(TPAs)_2(ClO_4)_2$	1575(s), 1555(sh), 1455(s)*, 1425(s)*	1100–1080(vs), 617(s)	1013(m)
$Ni(TPAs)_2(ClO_4)_2$	1575(s), 1550(m), 1455(s)*, 1420(s)	1100–1085(vs), 615(s)	1014(m)
$Cu(TPAs)_2(ClO_4)_2$	1580(s), 1555(sh), 1460(s)*, 1425(s)*	1100–1070(vs), 616(s)	1016(m), 1000(m)
$Zn(TPAs)_2(ClO_4)_2$	1580(s), 1560(sh), 1460(s)*, 1425(s)*	1100–1075(vs), 615(s)	1010(m)

[a] Absorptions (in cm^{-1}) were taken from spectra recorded as mineral oil mulls except those denoted by an *, which were recorded as hexachlorobutadiene mulls.

[b] w = weak, m = medium, s = strong and vs = very strong intensities; sh = shoulder.

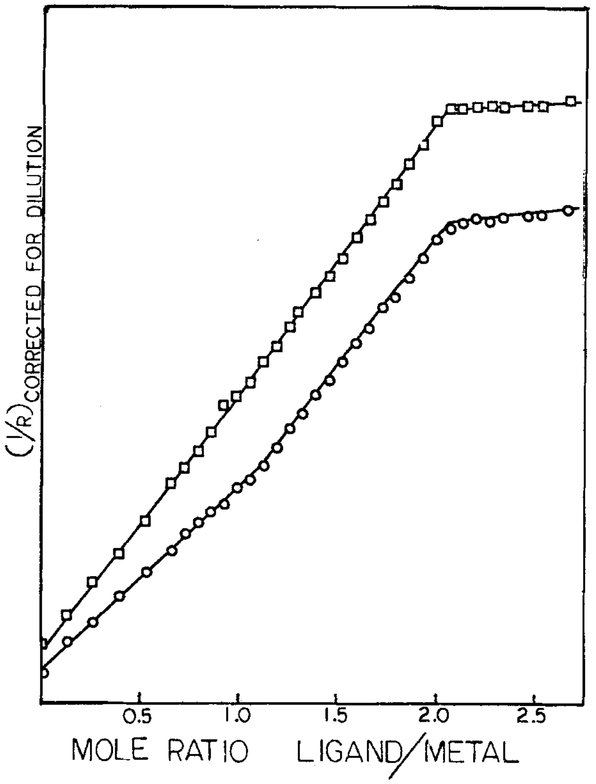


FIGURE 1 Conductivity titrations of metal(II) perchlorate with TPP
○ Co(II) with TPP
□ Zn(II) with TPP

tivities of the 2:1(L:M) complexes in acetonitrile (Table III) are within the range of typical 2:1 electrolytes. The Onsager limiting law[21]

$$\Lambda_{eq} = \Lambda_o - A\sqrt{C_{eq}}$$

where Λ_{eq} is the equivalent conductivity, Λ_o is the equivalent conductivity at infinite dilution, and C_{eq} is the equivalent concentration, has been used to demonstrate that only monomeric units are present in solution. The slope, A, taken from a plot of Λ_{eq} versus $\sqrt{C_{eq}}$ reflects the type of ionic species in solution. Experimental values of A are compared to the theoretical values of A calculated for 2:1 electrolytes (Table III). The close correspondence of calculated and experimental values establishes that the composition of the complexes in solution is the same as in the solid state, i.e, a $[M(TPX)_2]^{2+}$ cation and two ionic ClO_4^- anions.

The visible spectra of the colored complexes in acetonitrile (Table III, Figure 2) are consistent with a $[M(TPX)_2]^{2+}$ cation with all the pyridyl rings coordinated, in that electronic spectra can only be interpreted on the basis of an octahedral configuration around the metal ion. A Co(II) ion in an octahedral configuration normally exhibits three d–d transitions. The $[Co(TPX)_2]^{2+}$ bands at 455, 475, and 465 nm (Table 3) are assigned to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)(\nu_3)$ transition and the bands at 910, 1010, and 940 nm are assigned to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$ transition.[22] The assignment of the shoulder at ~535 nm found in each of the three complexes is not straight forward. Since the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(\nu_2)$ transition is a two-electron process, it is less probable that of a one-electron d–d transition[11] and thus is normally of very low intensity. It is also common to observe some structure on the ν_3 band at room temperature due to vibrational phenomena, spin-orbit coupling, low-symmetry splitting of the ${}^4T_{1g}(P)$ term, and/or transitions to doublet states.[23]

In order to determine whether these shoulders at ~535 nm are the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transitions, calculations described by Ballhausen[22] were made using ν_1 = 10,990, 9,900, and 10,640 cm^{-1} and ν_3 = 21,975, 21,050, and 21,500 cm^{-1} for $[Co(TPP)_2]^{2+}$ $[Co(TPPO)_2]^{2+}$, and $[Co(TPAs)_2]^{2+}$, respectively, and Dq values of 1,228, 1,114, and 1,191 cm^{-1} for TPP, TPPO, and TPAs were obtained. From the Dq values ν_2 was calculated to be 23,270, 21,040, and 22,550 cm^{-1} for $[Co(TPP)_2]^{2+}$, $[Co(TPPO)_2]^{2+}$, $[Co(TPAs)_2]^{2+}$, respectively. From Table 3, it is seen that these values differ from the position of the observed shoulders by 2,500 to

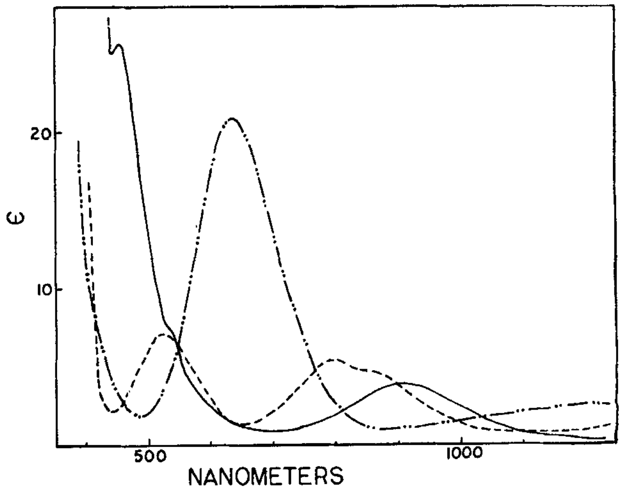


FIGURE 2 The visible spectra of $[M(TPP)_2](ClO_4)_2$
——— $[Co(TPP)_2](ClO_4)_2$
- - - - - $[Co(TPP)_2](ClO_4)_2$
$[Ni(TPP)_2](ClO_4)_2$
—·— $[Cu(TPP)_2](ClO_4)_2$

TABLE III
Conductivity data and electronic spectra of $[M(TPX)_2](ClO_4)_2$ in acetonitrile

	Λ_m^a (ohms^{-1} cm^2 mole^{-1})	Λ_o (ohms^{-1} cm^2 eq^{-1})	A_{exp}	A_{theor}^c	λnm(ε)[e]
$[Mn(TPP)_2](ClO_4)_2$	311	185.9	695	721	–
$[Co(TPP)_2](ClO_4)_2$	310	186.6	709	723	455(26), 535(sh)[d], 910(4)
$[Ni(TPP)_2](ClO_4)_2$	309	187.0	737	724	522(7), 795(5), 875(sh)[d]
$[Cu(TPP)_2](ClO_4)_2$	306	191.2	840	732	635(21)
$[Zn(TPP)_2](ClO_4)_2$	312	186.8	695	723	–
$[Mn(TPPO)_2](ClO_4)_2$	298	181.6	731	712	–
$[Co(TPPO)_2](ClO_4)_2$	296	172.5	676	694	475(18), 535(sh)[d], 1010(5)
$[Ni(TPPO)_2](ClO_4)_2$	294	180.1	757	709	555(13), 800(sh)[d],, 900(8)
$[Cu(TPPO)_2](ClO_4)_2$-green	278	180.1	748	709	633(27)
$[Cu(TPPO)_2](ClO_4)_2$-blue	338	209.7	903	771	680(63)
$[Zn(TPPO)_2](ClO_4)_2$	301	182.0	708	713	–
$[Mn(TPAs)_2](ClO_4)_2$	311	185.3	670	720	–
$[Co(TPAs)_2](ClO_4)_2$	311	187.5	736	725	465(16), 530)(sh)[d], 940(4)
$[Ni(TPAs)_2](ClO_4)_2$	298	184.1	797	718	550(9), 800(sh)[d], 880(6)
$[Cu(TPAs)_2](ClO_4)_2$	311	185.5	685	720	645(22)
$[Zn(TPAs)_2](ClO_4)_2$	312	194.9	881	740	–

[a] Solutions *ca.* 10^{-3} *M.*
[b] From a least-square analysis of seven points.
[c] Values used in the calculation: $\lambda^\circ_{ClO_4^-} = 103.4$, dielectric constant = 36.0, viscosity = 3.448 millispoise, T = 298°K
[d] sh = shoulder
[e] ε = molar absorptivity

6,500 cm^{-1} indicating that the shoulders are probably not this transition. Theoretically, the ν_2/ν_1 transition energy ratio is nearly invariant at 2.1–2.2 for octahedral Co(II) complexes[23] and the ratio between the calculated ν_2 transition and the observed ν_1 transition is 2.12 ± 0.01 for the three TPX complexes. The shoulders most likely arise through the presence of spin forbidden transitions to doublet states made possible by "intensity stealing" from the allowed band.[23]

A Ni(II) ion in an octahedral configuration also normally has three d–d transitions. As is the case in these complexes, the highest-energy transition, $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$, is often found in the ultraviolet region and thus is obscured by intense overlapping ligand bands. The bands at 522, 555, and 500 nm can be assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition (ν_2).[22,23] The double peak appearance of the low-energy transition, $^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, has been observed for other Ni(II) complexes[24] with various nitrogen-containing ligands and has been attributed to the appearance of a fourth transition, $^3A_{2g} \rightarrow {}^1E_g(D)$.[25,26] Busch, *et al.*[24] have suggested that the $^1E_g(D)$ state should be of lower energy than the $^3T_{2g}(F)$ state for Dq values in excess of 1200 cm^{-1}. It is also expected that the transition to the $^3T_{2g}$ state should be of greater intensity than the transition to the $^1E_{2g}(D)$ state. With this criteria in mind, the bands at 795, 900 and 800nm for the TPP, TPPO, and TPAs complexes are assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transition. This gives Dq values of 1,258, 1,110, and 1,136 cm^{-1} for TPP, TPPO, and TPAs, in good qualitative agreement with those previously calculated from the Co(II) spectra. The strong electron-withdrawing effect of the oxygen atom can be seen from a comparison of the Dq value of TPP with that of TPPO, since the Dq value reflects the availability of electron-density at the coordination site.

A Cu(II) ion normally exhibits a Jahn-Teller distortion. Consequently the assignment of bands is complicated since the shape and number of bands observed will be dependent upon the extent of this distortion.[11] Normally, only one band or a band with structure is seen at room temperature. The room temperature solution absorptions for the $[Cu(TPX)_2](ClO_4)_2$ complexes, except $[Cu(TPPO)_2](ClO_4)_2$-blue, appear as nearly symmetrical bands, indicating only minimal Jahn-Teller distortion. This is consistent with the infrared data which indicate nearly equivalent pyridines.

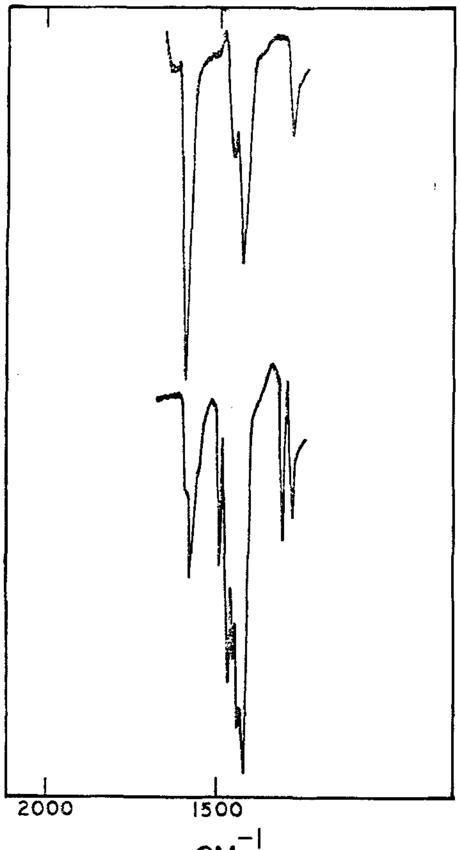


FIGURE 3 A comparison of the infrared spectra of $[Cu(TPPO)_2](ClO_4)_2$-green (top) and $[Cu(TPPO)_2](ClO_4)_2$-blue (bottom) between 1440 and 1600 cm^{-1}

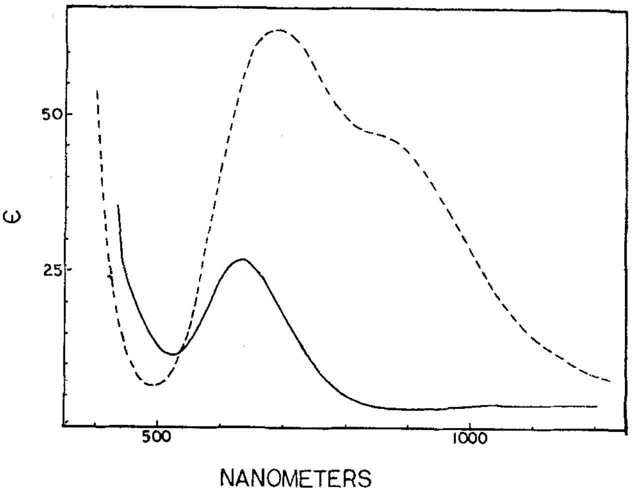


FIGURE 4 The visible spectra of the two $[Cu(TPPO)_2](ClO_4)_2$ complexes in acetonitrile

———— $[Cu(TPPO)_2](ClO_4)_2$-green

– – – – $[Cu(TPPO)_2](ClO_4)_2$-blue

The $[Cu(TPPO)_2](ClO_4)_2$-blue complex is the only complex isolated which shows a large deviation in physical data from the remaining complexes. The presence of at least eight rather than four $\nu_{(C=C)}$, $\nu_{(C=N)}$ bands between 1440 and 1600 cm^{-1} (Figure 3) indicates the non-equivalence of the pyridyl rings[15] and bidentate behaviour for the ligand must be suspected. The visible absorption spectra, when compared to that for $[Cu(TPPO)_2](ClO_4)_2$-green (Figure 4), has a large shoulder on the low-energy side indicating a considerable distortion of the symmetry around the Cu(II) ion. The slope of the A_{eq} versus $\sqrt{C_{eq}}$ for this complex (Table III) is substantially higher than that predicted for a monomer, indicating appreciable association in solution.

McWhinnie, *et al.*,[4] have reported both tridentate and bidentate behaviour for TPAm in Cu(II) complexes. However, when bidentate behaviour was indicated, the infrared spectra also indicated coordinated ClO_4^- by the splitting of ν_3(1100 cm^{-1}) and the increased intensity of ν_1(930 cm^{-1}). No such coordination is observed for $[Cu(TPPO)_2](ClO_4)_2$-blue. Thus, the Cu(II) coordination in this complex must be considered as either a strongly tetragonally distorted octahedron or as a square planar configuration. In either case, association of the unique pyridyl group with the axial positions of a second Cu(II) may explain the high value for the slope from the Onsager conductivity data (Table III). In solution, association between the axial positions of the Cu(II) and the oxygen of the P=O group may also occur, although there is no evidence for this in the solid state as indicated by the increased frequency of the P=O stretch.

CONCLUSIONS

The ligands TPAm, TPP, TPPO, and TPAs coordinate to first row transition metal perchlorates as symmetric tridentates. The central apical ligand-atom has little or no effect on the pyridyl coordination or metal electronic absorptions. This might be expected on the basis of the distance between the metal and apical atom. However, we find that the apical atom effect is large is some cases where $[M(TPX)_2]^{n+}$ is oxidized or reduced. Also in the complexes (TPX)Mo-

$(CO)_3$, both the visible-U.V. spectra and the mass spectral fragmentation patterns are dependent on the apical atom of the ligand. These studies will be covered in a later report.

ACKNOWLEDGEMENTS

This work was supported in part by a grant to D.A.Z. from the Petroleum Research Fund, administered by the American Chemical Society. R.K.B. wishes to acknowledge his gratitude for an NDEA pre-doctoral fellowship.

REFERENCES

1. Presented in part at the American Chemical Society Southeastern Regional Meeting, Richmond, Va., 1969; taken from the Ph.D. thesis of R.K.B., University of Alabama, Jan., 1973.
2. Address correspondence to this author at Thomas More College, P.O. Box 85, Covington, KY 41017.
3. J. R. Ferraro, D. W. Meek, E. C. Siniec, and A. Quattorchi, *J. Amer. Chem. Soc.*, 93, 3862 (1971) and references therein.
4. W. R. McWhinnie, G. C. Kulasingam, and J. C. Draper, *J. Chem. Soc. A*, 1199 (1966).
5. G. C. Kulasingam and W. R. McWhinnie, *J. Chem. Soc. A*, 1253 (1967).
6. G. C. Kulasingam and W. R. McWhinnie, *J. Chem. Soc. A*, 254 (1968).
7. R. C. Poller, J. N. R. Ruddick, M. Thevarasa, and W. R. McWhinnie, *J. Chem. Soc. A*, 2327 (1969).
8. W. R. McWhinnie, R. C. Poller, and M. Thevarasa, *J. Chem. Soc. A*, 1671 (1967).
9. R. R. Berrett, B. W. Fitzsimmons, and A. A. Owusu, *J. Chem. Soc. A*, 1575 (1968).
10. J. E. Huheey, *Inorganic Chemistry* (New York: Harper and Row Publishers, 1972).
11. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (New York: Interscience Publishers, 1966).
12. E. Plazek and R. Tyka, *Zeszyty Nauk. Politech. Wroclaw., Chem.*, 4, 79 (1957); *CA 52*: 20156c.
13. F. G. Mann and J. Watson, *J. Org. Chem.*, **13**, 502 (1948).
14. D. A. Baldwin, A. B. P. Lever, and R. V. Parish, *Inorg. Chem*, 8, 107 (1969) and references therein.
15. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy* (New York: Academic Press, 1963).
16. P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).
17. S. P. Sinha, *Spectrochem. Acta*, **20**, 879 (1964).
18. B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).
19. F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).
20. J. V. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *J. Amer. Chem. Soc.*, 76, 5185 (1954).
21. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (New York: Reinhold Publishing Corp., 1958).
22. C. J. Ballhausen, *Introduction to Ligand Field Theory* (New York: McGraw-Hill Book Co., 1962).
23. A. B. P. Lever, *Inorganic Electronic Spectroscopy* (New York: Elsevier Publishing Co., 1968).
24. M. A. Robinson, J. D. Curry and D. H. Busch, *Inorg. Chem.*, 2, 1178 (1963).
25. C. K. Jorgensen, *Acta Chem. Scand.*, 9, 1362 (1955).
26. A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N.Y.)*, 6, 134 (1959).