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Some Observations on Triazene 1-Oxide Complexes of Bivalent Nickel, Palladium and Copper

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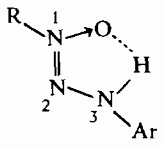
Several triazene 1-oxide chelates of nickel(II), palladium(II) and copper(II) are described. These complexes show crystal field bands at unusually low energies. The nickel(II) complexes are uniformly diamagnetic in the solid state. However, in the solution (benzene, chloroform) phase a slight paramagnetism develops in all nickel(II) complexes except those having a non-coordinating substituent in the ortho *position of the benzene ring. The pmr spectra of the partially paramagnetic complexes show small contact shifts. These shifts can be qualitatively interpreted on the basis of the existence of unpaired spin density in a π-orbital. The palladium(II) complexes having a substituent in the* ortho *position of the benzene ring exist in isomeric forms. In one case the isomeric forms have abeen separated by chromatography on a column of alumina. The copper(II) complexes have normal magnetic moments.*

Introduction

On the basis of infrared data, the product of the reaction of a diazonium salt (ArN_2X) with a substituted hydroxylamine (RNHOH) has been shown to have the triazene 1-oxide structure *1*.[1,2] Triazene 1-oxides act as versatile ligands forming nonelectrolytic chelates *2* with many metal ions. Whereas the syntheses of a variety of complexes and their usefulness in analytical separations have been described,[3,4,5] few results are available on structural and spectroscopic aspects of these complexes. Recently the syntheses, stereochemistry and electronic spectra of some cobalt(III),[2] rhodium(III)[6] and chromium(III)[6] chelates (n = 3, in *2*) were reported from this laboratory. In this paper several bis complexes (n = 2, in *2*) of nickel(II), palladium(II) and copper(II) are examined magnetically and spectroscopically. Some interesting observations are reported the structural bases of which are not quite clear to us at present. In what follows, the complexes *2* (n = 2) will be abbreviated as $(R-Ar)_2M$. Positions of substituents in the aromatic ring are indicated by using prefixes *o, m, p, m'* and *o'* which are counted with reference to the N–C(Ar) bond.



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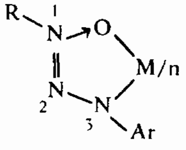

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Experimental Section

Preparation of compounds. The ligands were synthesized in the usual way.[2] The complexes could be prepared[4] as crystalline solids by reacting a hot alcoholic solution of the ligand (0.02 mole) with an aqueous solution of the appropriate metal acetate (0.01 mole). Recrystallizations were carried out from acetone or ethanol.

Cromatographic separation of $(Me-o-Tolyl)_2Pd$ into isomeric forms. 0.58 g of the crude complex was eluted with 50:50 benzene-hexane mixture from a column of alumina (80-200 mesh; 60 g). From the band which moved with this solvent were isolated 0.14 g of shining violet crystals, mp, 217-218°. The eluant was then changed to pure benzene and a second band which had already formed near the top of the column was washed out completely. By the removal of solvent, 0.36 g (mp, 185-86°) of the dark violet isomer was obtained.

Electronic Spectra were measured on a Cary 14 Recording Spectrophotometer having thermostated cell compartments. *Proton magnetic resonance* measurements were done on a Varian HR–100 spectrometer using tetramethylsilane as the internal standard. *Bulk susceptibility* measurements were done using a sensitive Gouy balance described elsewhere.[7] $CoHg(SCN)_4$ and distilled water were used as the standards for measurements on solids and solutions respectively. Some solution measurements were checked by Evan's method.[8]

Molecular weight measurements were carried out on a Vapour Pressure Osmometer Model 301A (Me-

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(1) T. Mitsuhasi, Y. Osamura, and O. Simamura, *Tetrahedron Letters*, 2593 (1965).

(2) A. Chakravorty, B. Behera, and P.S. Zacharias, *Inorg. Chimica Acta*, *2*, 85 (1968).

(3) E. Bamberger, *Ber.*, *29*, 103 (1896); E. Bamberger and E. Renauld, *ibid.*, *30*, 2278 (1897).

(4) M. Elkins and L. Hunter, *J. Chem. Soc.*, 1346 (1938).

(5) D.N. Purohit, *Talanta*, *14*, 353 (1967).

(6) B. Behera and A. Chakravorty, *J. Inorg. Nucl. Chem.*, *31*, 1791 (1969).

(7) T. S. Kannan and A. Chakravorty, *Inorg. Chem.*, *9*, 1153 (1970).

(8) D.F. Evans, *J. Chem. Soc.*, 2003 (1959).

Table I. Characterization of Compounds 2

Compound R	Ar		Formula	Mp, °C[a]	%C Calcd.	%C Found	%H Calcd.	%H Found	%N Calcd.	%N Found
CH_3	C_6H_5	Ni	$C_{14}H_{16}N_6O_2Ni$	179-80	46.82	46.79	4.46	4.54	23.42	23.49
CH_3	$C_6H_4CH_3(o)$	Ni	$C_{16}H_{20}N_6O_2Ni$	203-04	49.65	49.79	5.17	5.37	21.72	22.03
CH_3	$C_6H_4CH_3(m)$	Ni	$C_{16}H_{20}N_6O_2Ni$	177-78	49.65	49.84	5.17	5.30	21.72	21.45
CH_3	$C_6H_4CH_3(p)$	Ni	$C_{16}H_{20}N_6O_2Ni$	220	49.65	49.68	5.17	5.03	21.72	21.87
CH_3	$C_{10}H_7(\alpha)$	Ni	$C_{22}H_{20}N_6O_2Ni$	213-14	57.54	57.40	4.36	4.59	18.74	18.40
CH_3	$C_6H_3(CH_3)_2(o, m')$	Ni	$C_{18}H_{24}N_6O_2Ni$	212	52.10	52.20	5.79	5.71	20.26	20.30
C_2H_5	C_6H_5	Ni	$C_{16}H_{20}N_6O_2Ni$	156-58	49.65	49.42	5.17	5.31	21.72	21.66
C_3H_7	C_6H_5	Ni	$C_{18}H_{24}N_6O_2Ni$	131-32	52.22	52.42	5.78	5.93	20.26	20.44
CH_3	C_6H_5	Cu	$C_{14}H_{16}N_6O_2Cu$	156-57	46.23	46.79	4.40	4.60	23.12	22.79
CH_3	$C_6H_4CH_3(o)$	Cu	$C_{16}H_{20}N_6O_2Cu$	168-69	49.05	49.20	5.11	5.26	21.46	21.17
CH_3	$C_6H_4CH_3(m)$	Cu	$C_{16}H_{20}N_6O_2Cu$	138-39	49.05	49.40	5.11	4.80	21.46	21.55
CH_3	$C_6H_4CH_3(p)$	Cu	$C_{16}H_{20}N_6O_2Cu$	186-87	49.05	49.21	5.11	4.90	21.46	21.44
C_2H_5	C_6H_5	Cu	$C_{16}H_{20}N_6O_2Cu$	135-36	49.05	49.42	5.11	5.24	21.46	21.71
CH_3	C_6H_5	Pd	$C_{14}H_{16}N_6O_2Pd$	207-08	41.34	41.78	3.93	4.10	20.67	20.64
CH_3	$C_6H_4CH_3(m)$	Pd	$C_{16}H_{20}N_6O_2Pd$	186-87	44.20	44.78	4.60	4.40	19.34	19.54
CH_3	$C_6H_4CH_3(p)$	Pd	$C_{16}H_{20}N_6O_2Pd$	230	44.20	44.35	4.60	4.91	19.34	19.56
CH_3	$C_6H_4CH_3(o)$	Pd { A[b]	$C_{16}H_{20}N_6O_2Pd$	218	44.20	44.71	4.60	4.79	19.34	19.14
		B[b]	$C_{16}H_{20}N_6O_2Pd$	185	44.20	44.30	4.60	4.62	19.34	19.72
CH_3	$C_6H_4Cl(o)$	Pd[c]	$C_{14}H_{14}N_6O_2Cl_2Pd$	192-93	35.34	35.67	2.94	3.02	17.67	17.05
CH_3	$C_6H_4OCH_3(o)$	Pd[c]	$C_{16}H_{20}N_6O_4Pd$	194	41.17	41.83	4.29	4.35	18.01	17.82
CH_3	$C_6H_3(CH_3)_2(o, m')$	Pd[c]	$C_{18}H_{24}N_6O_2Pd$	203-04	46.72	46.32	5.19	5.43	18.17	18.03
CH_3	$C_6H_3ClCH_3(o, m')$	Pd[c]	$C_{16}H_{1}\ N_6O_2Pd$	181-82	38.15	38.36	3.58	3.86	16.69	16.31
CH_3	$C_6H_3(CH_3)_2(o, o')$	Pd	$C_{18}H_{24}N_6O_2Pd$	220-21	46.72	47.01	5.19	5.50	18.17	18.51
C_2H_5	C_6H_5	Pd	$C_{16}H_{20}N_6O_2Pd$	213-14	44.20	44.70	4.60	4.51	19.34	18.89

[a] All melting points reported in this table are uncorrected. [b] Two isomeric forms. Isomer more easily eluted from chromatography column is A. [c] This is probably an isomeric mixture (refer to text).

Table II. Osmometric Molecular weight of some Compounds of Type 2[a] in Benzene[b] at 310°K

Compound R	Ar	M	Molecular weight Calcd.	Molecular weight Found
CH_3	C_6H_5	Ni	359	369
CH_3	$C_6H_4CH_3(m)$	Ni	387	386
C_2H_5	C_6H_5	Ni	387	391
CH_3	C_6H_5	Cu	364	360
CH_3	C_6H_5	Pd	406	405
CH_3	$C_6H_4Cl(o)$	Pd	475	466
CH_3	$C_6H_4OCH_3(o)$	Pd	466	458
CH_3	$C_6H_4CH_3(o)$	Pd { A[c]	434	439
		B	434	429

[a] Refer to compound figure number in the body of the text. [b] Solute concentration: 0.02-0.04 *M*. [c] More easily eluted isomer.

chrolab Inc.) in benzene using solute concentrations of the order of 10^{-2} *M*.

Results and Discussion

Syntheses of chelates. Characterization data of some of the chelates prepared during this investigation are set out in Table I. Some of the copper(II) and nickel(II) complexes appearing in this Table are already reported in early literature.[4] For the sake of completeness we have included them in Table I. The synthetic procedure involves straightforward mixing of reagents as prescribed by Elkins and Hunter.[4] The chelates are soluble in many organic solvents. They are essentially monomolecular in the solution phase. Some selected molecular weight data in benzene are shown in Table II.

Nickel(II) complexes. No crystal structure data is available on any of the complexes described here. However, the nickel(II) complexes are uniformly diamagnetic in the crystalline state and this suggests a grossly planar NiN_2O_2 coordination sphere. Each complex could be isolated in only one isomeric form which presumably has the *trans* geometry. Overcrowding of the two aryl groups is likely to make the *cis* form unstable.

In the crystalline state the nickel(II) complexes show a prominent band in the visible region at ~13,500 cm^{-1}. The same band is also observed in the solution (benzene or chloroform) phase. Some results are shown in Table III and Figure 1. On the basis of its intensity the 13,500 cm^{-1} band may be attributed to a ligand field transition. In idealised D_{2h} symmetry a probable assignment is $^1A_{1g} \rightarrow {}^1B_{1g}$ $(d_{xy} \rightarrow d_{x^2-y^2})$. This assignment is based on analogy with salicylaldimine complexes of Ni^{II} which also have a NiN_2O_2 coordination sphere and show one ligand field band[9] (16,000-16,500 cm^{-1}) in the visible region. However, the energy of the band in the triazene 1-oxide chelates in unusually low compared to that of salicyaldimines. In fact few grossly planar Ni^{II} chelates other than those derived from dithiols[10,11] and aminotroponeimines[10,12] show singlet-singlet bands of ligand field origin at such low energies. The band at ~27,700 cm^{-1} is probably a metal-perturbed transition centered mainly on the ligand (Table III).

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(9) J. Ferguson *J. Chem. Phys.*, *34*, 611 (1961); B. Bosnich, *J. Am. Chem. Soc.*, *90*, 627 (1968).

(10) In maleodinitriledithiolatonickel(II) dianion a band at 11,690 cm^{-1} has the symmetry of the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. However, the orbitals involved are very far from being localized on the nickel(II) atom[11]. In the aminotroponeimineate chelates[12] the singlet-singlet band appears at ~12,500 cm^{-1}.

(11) S.I. Schupack, E. Billig, R.J.H. Clark, R. Williams, and H.B. Gray, *J. Am. Chem. Soc.*, *86*, 4594 (1964).

(12) D.R. Eaton, W.D. Phillips, and D.J. Caldwell, *ibid.*, *85*, 397 (1963).

Table III. Frequencies (ν, cm^{-1}) and Extinction Coefficients (ε, $l.mol^{-1}.cm^{-1}$) of Electronic bands of Nickel(II) and Palladium(II) Complexes in Benzene at room Temperature (300°K)

Compound R	Ar	M	ν(ε)
CH_3	C_6H_5	[a]	32,260 (21,850)
CH_3	C_6H_5	Ni [b]	9350 (1.1)[c]; 13,510 (107)[d]; 27,780 12,500)[e]
CH_3	$C_6H_4CH_3(o)$	Ni [f]	13,890 (104)[d]; 28,570 (8509)[e]
CH_3	$C_6H_4CH_3(m)$	Ni	9260 (2 at 333°K)[c]; 13,510 (104 at 333°K)[d] (1.5 at 308°K) (106 at 303°K) (1 at 263°K) (111 at 262°K) 27,780 (12,900)[e]
CH_3	C_6H_5	Pd	18,520 (254)[g]; 27,780 (21,420)[h]
CH_3	$C_6H_4CH_3(p)$	Pd	18,520 (266)[g]; 27,780 (15,950)[h]
CH_3	$C_6H_4Cl(o)$	Pd	18,520 (147)[g]; 29,000 (14,200)[h]
CH_3	$C_6H_4OCH_3(o)$	Pd	18,690 (217)[g]; 28,570 (15,500)[h]
CH_3	$C_6H_4CH_3(o)$	Pd A	18,500 (298)[g]; 28,600 (13,460)[h]
		Pd B	18,500 (145)[g]; 28,600 (10,260)[h]

[a] Free ligand. [b] Spectrum in chloroform: 9350 cm^{-1} (1.4); 13,510 cm^{-1} (109); 27,780 cm^{-1} (9830). [c] Solute concentration $\sim 0.1\ M$. [d] Solute concentration is $\sim 5 \times 10^{-3}\ M$. [e] Solute concentration is $\sim 5 \times 10^{-5}\ M$. [f] No band observed at ~9300 cm^{-1}. [g] Solute concentration is $\sim 3 \times 10^{-3} M$. [h] Solute concentration is $\sim 4 \times 10^{-5}\ M$.

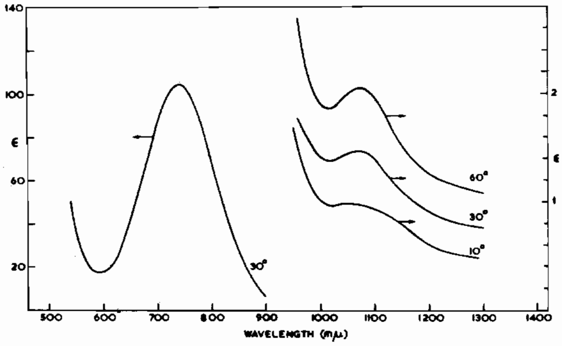

Figure 1. Electronic spectra of (Me—*m*—Tolyl)$_2$Ni in benzene solution at several temperatures. For clarity spectrum at only one temperature is shown for the band at higher energy.

A careful examination of concentrated solutions of the chelates, (Me—Ph)$_2$Ni, (Et—Ph)$_2$Ni and (Me—*m*—Tolyl)$_2$Ni, reveals the existence of a weak band at ~9300 cm^{-1} (Table III, Figure 1). The intensity of this band increase with increase in temperature and at a given temperature Beer's law is strictly obeyed (concentration range investigated: 0.01195 *M*—0.1193 *M* in the case of (Et—Ph)$_2$Ni). In the complexes having a non-coordinating substituent[13,14] in the *ortho* position of the benzene ring, the ~9300 cm^{-1} feature is absent. Examples are, (Me—*o*—Tolyl)$_2$Ni and (Me—α—Naphthyl)$_2$Ni. The ~9300 cm^{-1} band appears to be associated with a paramagnetic species since all complexes which show this band are found to be feebly paramagnetic (μ_{eff}, 0.6—0.7 BM) in benzene or chloroform solution.

The partially paramagnetic nickel(II) complexes show characteristic, though small, contact shifts[15] for the proton resonance signals. Some selected data are presented schematically in Figure 2. As a result of the contact shifts the spectra of the aromatic protons are essentially first order in spin-spin structure. This together with intensity considerations leads to straightforward and unequivocal assignment of the signals. The observation of a single signal for each type of protons clearly demonstrates that the diamagnetic and paramagnetic molecules are interconverting at a rate which is fast by pmr time scale.

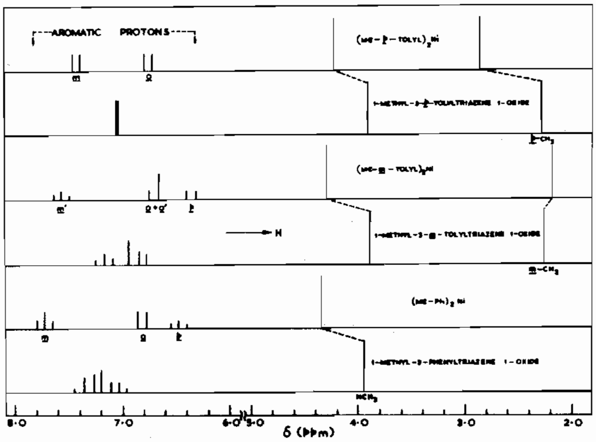

Figure 2. Proton magnetic resonance spectra (schematic) of some ligands and their nickel(II) complexes in $CDCl_3$.

An examination of Figure 2 shows that the *o*- and *p*-protons systematically show positive contact shifts,[16] while the *m*-protons show negative contact shifts. Another significant observation is that in (Me—*m*—Tolyl)$_2$Ni the *m*—CH_3 signal has a positive contact shift while in (Me—*p*—Tolyl)$_2$Ni the contact shift of the *p*—CH_3 signal is negative. The NCH_3 signal undergoes a negative contact shift in all the complexes.[17]

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(13) When the substituent is halogen, OCH_3 or SCH_3 psuedooctahedral species involving coordination of the substituent is obtained[14].

(14) P.S. Zacharias, B. Behera, and A. Chakravorty, *J. Am. Chem. Soc.*, *90*, 7363 (1968); and unpublished investigation.

(15) D.R. Eaton and W.D. Phillips, *Advan. Magnetic Resonanee*, *1*, 103 (1965).

(16) The contact shift is positive when the resonance signal of the paramagnetic complex is at a higher field than that of the corresponding diamagnetic material (free ligand, or its zinc(II) or palladium(II) complexes).

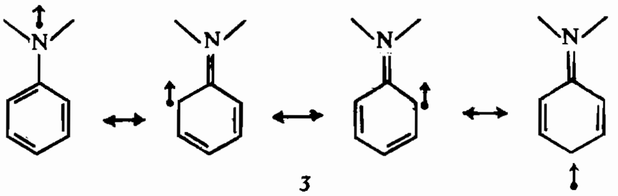
(17) In (Me-*o*-Tolyl)$_2$Ni, in common with other diamagnetic chelates the N-CH_3 signal undergoes a slight shift to higher field. All the diamagnetic chelates in common with the free ligands show a complex pattern in the aromatic region which we did not attempt to analyse.

Table IV. Frequencies (ν, cm^{-1}) and Extinction Coefficients (ε, l.mol^{-1}. cm^{-1}) of Electronic bands and Magnetic Moments of Copper(II) Complexes (300°K)

Compound R	Ar	$\nu(\varepsilon)$ in benzene [a]	$\nu(\varepsilon)$ in Pyridine [b]	μ^{c}_{eff} (BM)
CH_3	C_6H_5	11,000 (69); 24,390 (700), 31,250 (32,000)	10,870 (65); 30,800 (26,200)	1.86
CH_3	$C_6H_4CH_3(o)$	11,100 (97); 25,000 (978)	11,100 (90); 25,000 (1307); 32,260 (14,800)	1.84
CH_3	$C_6H_4CH_3(m)$	10,800 (81); 24,300 (600)[d]; 31,250 (12,900)	10,800 (73); 30,770 (25,550)	1.83
CH_3	$C_6H_4CH_3(p)$	10,800 (81); 24,300 (729)[d]; 29,000 (32,000)	10,800 (73); 31,750 (19,300)	[e]

[a] All complexes show an additional shoulder at ~18,200 cm^{-1}. [b] All complexes show an additional shoulder at ~18,200 cm^{-1}. [c] Magnetic moments in the solid state. [d] Shoulder. [e] Not measured.

The contact shifts undoubtedly arise due to delocalization of unpaired spins from the metal into the ligand system. The observed pattern of contact shifts of the aromatic protons is in accord[15] with the existence of unpaired spin in a π–orbital of the aromatic system. The simplest possible mechanism of spin delocalization is *via* the nitrogen (position 3) atom (ligand-to-metal charge transfer) leaving an α-spin on this atom. This spin can travel to *o*- and *p*-positions by direct delocalization in the odd-alternant radical shown as a resonance hybrid in 3.



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The consequent positive spin densities at the *o*- and *p*-carbon atoms lead to the positive contact shifts for protons directly attached to these positions and to the negative contact shift of hyperconjugated *p*–CH_3 protons. The negative spin density at the *m*-carbon atom can arise as usual from spin correlation effects.

The origin of the partial paramagnetism remains obscure for the present. Several possibilities, *viz.*, (1) solute-solute and/or solute-solvent association resulting in planar($S = O$) - pseudooctahedral($S = 1$) equilibrium, (2) planar($S = O$) - tetrahedral($S = 1$) equilibrium, (3) planar($S=O$)-planar($S=1$) equilibrium, were considered. However, none of these models can explain all of the observed results. This aspect will be dealt in details later.

Palladium(II) complexes. First the complexes without substituents in the *o*-position will be considered. They are generally isomorphous with the corresponding nickel(II) complexes. The structure of one complex *viz.*, (Ph–Ph)$_2$Pd has been solved[18] by X-ray crystallography. As expected it has a grossly planar *trans*–PdN_2O_2 coordination sphere. The palladium(II) complexes show a band at 18,500 cm^{-1} (Table III) which probably has the same assignment as the 13,500 cm^{-1} band of the nickel(II) complexes. Their nmr spectra are normal.

More interesting is the behaviour of complexes carrying a substituent (CH_3, Cl, OCH_3) in the *o*-position. Their pmr spectra show two different signals for each group of protons corresponding to two isomeric species. In the case of the complex (Me–*o*–Tolyl)$_2$Pd the two isomers could be easily separated[19] by chromatography on alumina. The less easily eluted isomer (isomer B) has the lower melting point (185°). It melts, then solidifies due to B→A conversion and then remelts at 218°, the melting point of the A isomer. Both isomers are essentially monomolecular in the solution phase (Table II). Their electronic spectra are qualitatively similar but the intensities are very different (Table III). The chemical shifts of the NCH_3 and CCH_3 protons in deuterochloroform are as follows: A, NCH_3, 3.60; CCH_3 2.39; B, 3.78; 2.09 ppm fgrom tetramethylsilane. The A isomer alone is isomorphous with (Me–*o*–Tolyl)$_2$Ni We have not yet been able to arrive at any definite conclusions about the origin of this isomerism.[20]

Copper(II) complexes. Spectral and magnetic data for these complexes are shown in Table IV. The magnetic moments are close to those of other grossly planar copper(II) complexes having an N_2O_2 coordination sphere. In principle grossly planar copper(II) complexes may be expected to show three to four crystal field bands depending upon the exact molecular symmetry.[21] However, in many cases only one broad asymmetric feature is experimentally observed. The same applies to the present chelates. The observed band (in benzene solution) appears at unusually low energy (~11,000 cm^{-1}) in keeping with the trend already described in the case of Ni^{II} and Pd^{II} chelates. In pyridine solution the intensity of this band decreases, but the energy is only slightly affected.

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(18) E.F. Meyer, Jr., *Dissertation Abstr.*, *26*, 1368 (1965).

(19) Attempted separation was not successful in the case of (Me-*o*-Chlorophenyl)$_2$Pd. Probably the isomers interconvert too rapidly for chromatographic separation. In order to disprove the remote possibility that the complexes having no *ortho* substituents contain two stable isomers having idential chemical shifts, chromatography of (Me-*m*-Tolyl)$_2$-Pd was carried out. As expected only a single species was obtained.

(20) We strongly disfavour one possibility, *viz. cis-trans* isomerism of the coordination sphere PdN_2O_2. There is no reason why such isomerism should be observed only in the case of *o*-substituted complexes. We believe that both the isomers have essentially *trans* coordination spheres. It is significant that while (Me-*o,m*-Dimethylphenyl)$_2$Pd like (Me-*o*-Tolyl)$_2$Pd exists in two isomeric forms, the complex (Me-*o,o'*-Dimethylphenyl)$_2$Pd shows a single set of nmr signal implying the existence of only one form.

(21) A. Chakravorty and T.S. Kannan, *J. Inorg. Nucl. Chem.*, *29*, 1691 (1967); L.L. Funk and T.R. Ortolano, *Inorg. Chem.*, *7*, 567 (1968).

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