

Registry No. [Pt₃(NH₃)₆(OH)₃](NO₃)₃, 61951-02-8; *cis*-diaquodiammineplatinum(II) dinitrate, 52241-26-6.

Supplementary Material Available: A table of the moduli of the observed and calculated structure amplitudes (13 pages). Ordering information is given on any current masthead page.

References and Notes

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- (2) (a) McMaster University. (b) Michigan State University.
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- (4) (a) IR intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. (b) Raman intensities are relative to the strongest band at 540 cm⁻¹ with arbitrary intensity 10.
- (5) The indices refer to a cell with $a = 9.683$ (3), $b = 8.832$ (3), $c = 11.007$ (4) Å; $\alpha = 102.64$ (3), $\beta = 106.59$ (2), $\gamma = 81.30$ (2)°. This cell can be obtained from the cell used throughout the paper by the transformation matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 1 \end{bmatrix}$$

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Spectroscopic and Spectromagnetic Study of Trichloro(triphenylarsine)bis(*p*-tolyl isocyanide)osmium(III). Characterization of the Three Isomeric Forms

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The three isomeric forms of the compound [OsCl₃(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂] have been isolated and their probable structures deduced by comparative use of vibrational, electronic, and magnetic measurements. The ground-state configuration of osmium(III) ion in a low-symmetry field is proposed and the perturbing influence of the isocyanide ligand on the metal center is discussed. The differences in the electronic distribution of the isomeric species are also considered.

Compounds of general formula [OsX₃L₃] (X = Cl, Br, I; L = PR₃, AsR₃, SbR₃; R = alkyl, aryl), with D_{2h}, C_{3v}, and C_{2v} symmetry, have been described.^{1,2} Symmetries lower than C_{2v} are in general associated with the reduction of the osmium(III) ion, by reaction with carbon monoxide, nitrogen monoxide, alkyl or aryl isocyanide, etc.³⁻⁵ We now report that the reaction of [OsCl₃(AsPh₃)₃] with *p*-tolyl isocyanide gives the new compound [OsCl₃(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂], in three isomeric forms. The electronic d⁵ configuration allows the investigation of the symmetry of the ligand field in these species, the bond strength between the osmium atom and ligand molecules, and the strength of the C-N bond, by electronic and magnetic measurements.

Experimental Section

Preparation. A suspension of [OsCl₃(AsPh₃)₃]⁶ (700 mg, 0.576 mmol) and *p*-tolyl isocyanide (270 mg, 2.3 mmol) in benzene (50 mL) was refluxed until a red-orange solution was obtained (~5 h). Upon evaporation to ~30 mL and addition of methanol (~50 mL) a microcrystalline red-orange solid precipitated, which was a mixture of two structural isomers, I and II, with formula [OsCl₃(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂]. After filtration, the solution was evaporated to ~20 mL and a yellow-orange precipitate was obtained, which consisted of isomer III of [OsCl₃(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂] and small quantities of [OsCl₂(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂]. Analytical data are given in Table I.

The separation of isomers I and II was based on their differing solubilities in benzene. The solid mixture was treated with benzene (~4 mL) at room temperature; isomer II dissolved leaving as residue isomer I. Upon filtration isomer II precipitated from the benzene solution with the addition of methanol (~20 mL). The pure products

were obtained by repeating the separation process.

Isomer III was separated from [OsCl₃(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂] by dissolving the solid mixture in benzene, at room temperature (~4 mL); on addition of methanol (~20 mL) isomer III precipitated; it was purified by repeating the separation process. Solubility in a solvent less polar than methanol (benzene) follows the order I << II < III. Yields: I, 15%; II, 60%; III, ca. 25%.

Upon treatment of a benzene solution of the osmium(III) isomers with triphenylarsine and reflux for ~2 h, [OsCl₂(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂] was obtained, which precipitated as a green solid upon the addition of methanol.

Isomer I is unstable with respect to III, even in the solid state at room temperature; isomer III gave II after short refluxing in benzene.

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer; Raman spectra, on a Coderg PHO krypton laser instrument; and diffuse reflectance electronic spectra, on a Beckman DK-2A spectrophotometer. ESR spectra were recorded on a Varian 4502-11 spectrometer, and the *g* values were calculated by standardization with diphenylpicrylhydrazyl. The magnetic susceptibility measurements were performed by the Gouy method. The molecular weight measurements were carried out with a Hewlett-Packard 302B vapor pressure osmometer.

Results

Vibrational Spectra. The following regions were analyzed: (a) 2300-2000 cm⁻¹, diagnostic for the N-C stretching vibrations;⁷ (b) 600-400 cm⁻¹, diagnostic for the Os-C vibrations;⁸ (c) 400-200 cm⁻¹, related to the Os-Cl stretching vibrations.⁴

The absorption frequencies of the three isomers are reported in Table II; their possible structures are indicated in Figure 1.

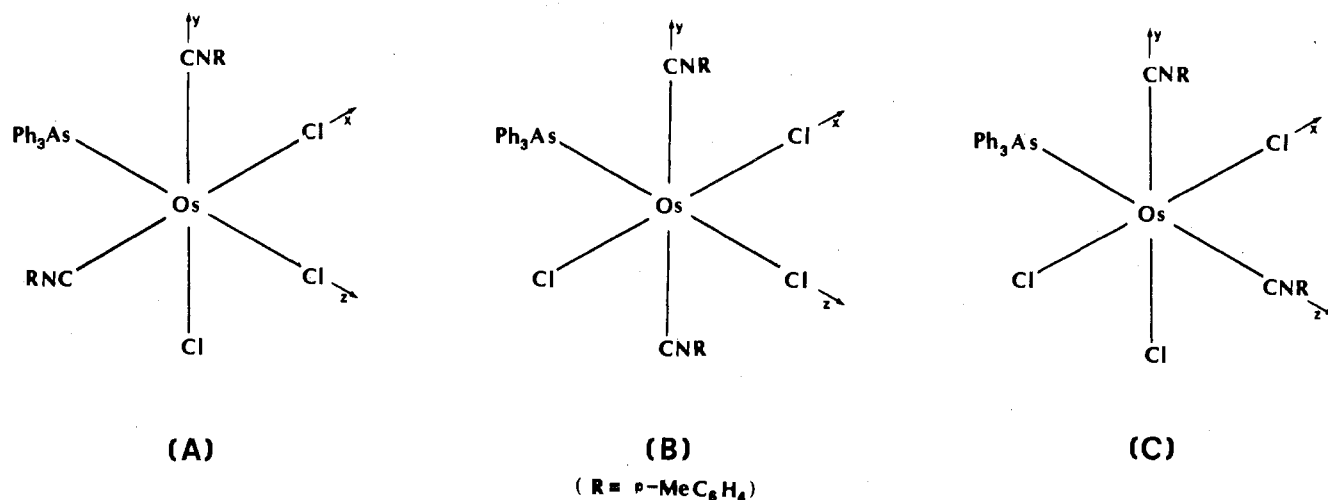
Table I. Analytical Data

Compd	% C		% H		% N		% Cl		Mol wt ^a	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$	48.80		3.47		3.35		12.68		836	
Isomer I		48.25		3.21		3.37		12.08		882
Isomer II		48.62		3.12		3.56		12.15		816
Isomer III		49.56		3.63		3.14		12.86		902
$[\text{OsCl}_2(\text{AsPh}_3)_2(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$	56.37	55.47	3.97	4.16	2.53	2.39	6.42	6.89	1107	1052

^a Chloroform solution.Table II. Infrared and Raman Absorption Frequencies (cm^{-1})^a

Compd	N-C	Os-C ^b [IR]	Os-Cl ^c [IR]
$[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$			
Isomer I	2189 w, 2150 s [IR] 2180 s, 2145 vw [R]	540 m, 490 m (515)	325 s, 315 s, 277 m (306)
Isomer II	2181 w, 2139 s [IR] 2176 s, 2135 vw [R]	540 m, 504 m (522)	326 s, 318 s, 293 s (312)
Isomer III	2189 w, 2150 s [IR] 2180 s, 2145 vw [R]	538 m, 500 m (519)	336 s, 316 s, 293 s (315)
<i>mer</i> - $[\text{OsCl}_3(\text{AsPh}_3)_3]$			337 s, 327 s, 313 s (325)
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{NC}^d$	2130 s [IR]		

^a IR = infrared spectra recorded in Nujol mull; R = Raman spectra recorded in solid powder; s = strong; m = medium; w = weak; vw = very weak. ^b Medium frequency of the Os-C vibrations in parentheses. ^c Medium frequency of the Os-Cl vibrations in parentheses. ^d Recorded in pure liquid phase.

Figure 1. Possible structures of $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$.

(a) In the N-C stretching region, the IR spectra of the isomers show two absorption bands, that at higher frequency being of lower intensity. The intensity ratios are reversed in the Raman spectra, so the bands at higher frequency may be assigned to the symmetrical N-C stretching modes and those at lower frequency to the asymmetrical modes, in accordance with the symmetry properties of our compounds (C_{2v} for structure B; C_s for A and C).

Symmetrical and asymmetrical N-C stretching frequencies of I and III are the same and are higher than those of II.

(b) The vibrational modes related to the osmium-carbon bonds lie in the same frequency range as the vibrations due to the arsine and isocyanide ligands. For this reason the spectra of the three isomers have been compared with that of $[\text{OsCl}_3(\text{AsPh}_3)_3]$ (Figure 2), and two new bands, whose positions were changed from one isomer to another, have been assigned to the osmium-carbon vibrations (Table II), in accordance with the symmetry properties of our compounds; their frequencies follow the order $\text{II} > \text{III} > \text{I}$ (the median value between the two frequencies has been taken as representative).

(c) The vibrations related to Os-Cl stretchings lie in the same frequency range as the absorptions due to the other

ligands; however the intensities of the metal-halogen stretching bands indicate three strong bands for all the isomers, as expected from the symmetry properties (see Figure 2). Clearly the bands of isomer I are different in shape and intensity from the very similar absorptions of II and III. If one takes the median frequency as representative, the trend is $\text{III} \approx \text{II} > \text{I}$. A higher median frequency is noted for $[\text{OsCl}_3(\text{AsPh}_3)_3]$.

Electronic and ESR Spectra. The isomeric forms of $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$ are low-spin paramagnetic compounds, with magnetic moment $\mu \approx 1.8 \mu_B$ at room temperature. This value is very similar to that for the compounds $[\text{OsX}_3\text{L}_3]$.^{1,2}

Major differences were noted in the ESR parameters of the isocyanide derivatives with respect to $[\text{OsX}_3\text{L}_3]$. The spectrum of $[\text{OsCl}_3(\text{AsPh}_3)_3]$ (Figure 3) shows two resonance types, corresponding to two different g values; the shape of the signals (which are similar to those of analogous compounds¹) suggests that a third principal component is present in the spectrum, at an unobservably high field; this is in accordance with a C_{2v} symmetry and a *mer* structure of $[\text{OsCl}_3(\text{AsPh}_3)_3]$.

The spectra of the polycrystalline samples of the isocyanide isomers (Figure 3) show three well-resolved g values, in agreement with the possible symmetries. The substitution of

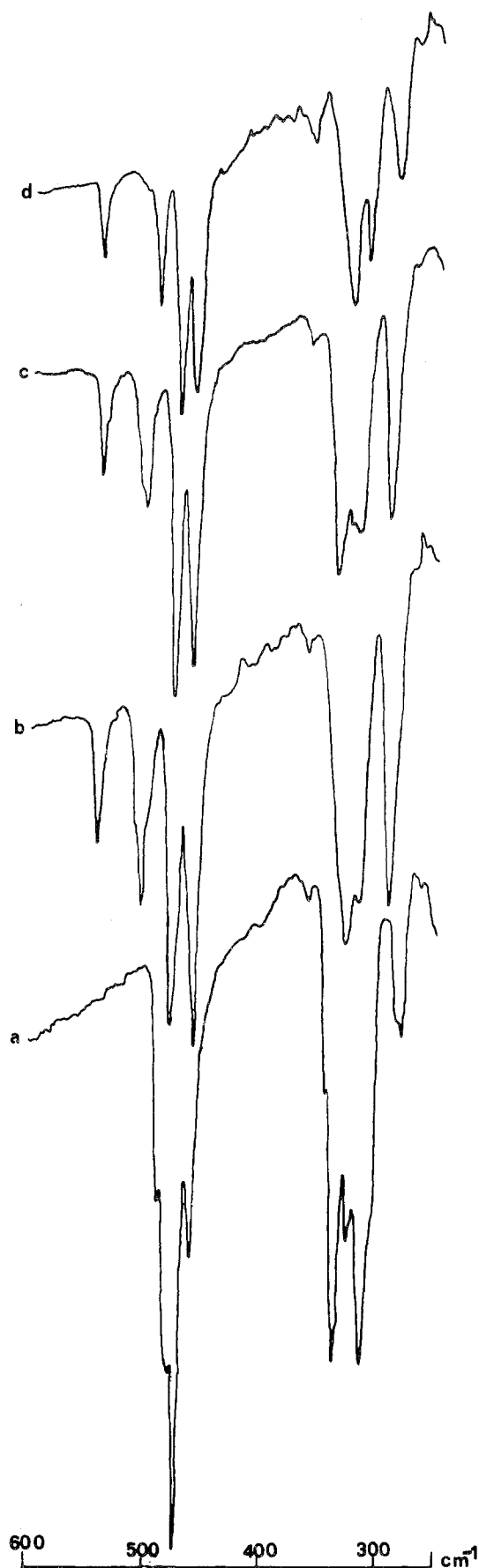


Figure 2. Infrared spectra, in Nujol mull, of (a) $[\text{OsCl}_3(\text{AsPh}_3)_3]$ and of $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$: (b) isomer II; (c) isomer III; (d) isomer I.

Table III. ESR Parameter Values and Electronic Absorption Frequencies ($\text{cm}^{-1} \times 10^3$)

Compd	g_1	g_2	g_3	ν_1	ν_2	ν_3
$mer\text{-}[\text{OsCl}_3(\text{AsPh}_3)_3]$	3.01	1.74		4.0	8.6	14.3
$[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$						
Isomer I	2.78	2.05	1.35	5.0	9.8	
Isomer II	2.78	2.15	1.4	5.1	9.5	
Isomer III	2.78	2.05	1.35	4.9	9.5	

two arsine ligands by two isocyanide molecules leads to the reduction of the g_1 value and to the increase of the g_2 and g_3 values. Small, reproducible increases of g_2 and g_3 (Table III) distinguish isomer II from isomers I and III. The value of g_1 is about the same; differences between g_1 and the other g components are smallest for isomer II. The values of the g components of the three isomers frozen in ethanol are identical with those in the polycrystalline phase.

The diffuse reflectance spectrum (Figure 4) of $[\text{OsCl}_3(\text{AsPh}_3)_3]$ shows three d-d absorptions in the near-infrared region; the spectra of the isocyanide isomers contain two bands. Therefore, the substitution of two arsines by two isocyanide molecules shifts the lowest frequency band of the parent compound to higher frequency, while that at highest frequency disappears. The energy difference between the two bands of the isocyanide isomers is least for isomer II and is comparable in isomers I and III (see Table III).

Discussion

The most probable structures of the three isomers can be assigned from the combination of the vibrational, electronic, and magnetic results, although none of the spectroscopic and spectromagnetic measurements is itself sufficient.

The results of the ESR analysis indicate that isomers I and III have identical molecular symmetries, while isomer II is different. Since these differences in magnetic parameters are noted also in solution, they can be attributed to differences in molecular structure. The most probable structure for II is thus B, which differs in symmetry from the other two.

The reflectance spectra show for II the lowest splitting between the two bands in the near-infrared region; since these bands can be attributed to electron transfers between linear combinations of d_{xz} , d_{yz} , and d_{xy} orbitals, the C_{2v} symmetry is confirmed.

The $\nu(\text{N-C})$ value shows that the N-C bond energy increases in all three isocyanide isomers with respect to the free isocyanide ligand, suggesting a poor $d_\pi\text{-}\pi^*$ overlap. The $d_\pi\text{-}\pi^*$ overlap is higher in isomer II, confirming the trans position of the two isocyanide ligands (structure B).

Isomers I and III, indistinguishable by their electronic and magnetic properties and by their $\nu(\text{N-C})$ vibrations, can be tentatively assigned on the basis of the Os-Cl vibrational properties. These are sensitive to the different electronic distribution in isomers I and III, depending on the σ -donor ability of the ligands in the trans position.⁴ So structure A can be assigned to isomer I, as the ligands trans to chlorine atoms have the lowest average σ donor (chlorine atoms in *fac* position). More σ donation is seen in isomer III, to which structure C (chlorine atoms in *mer* position) may be attributed. Structure A is also in accordance with the low solubility of I in benzene (the *fac* position of chlorines is consistent with higher polarity of A structure than of B and C structures) and with its tendency to be converted to III; structure B is consistent with the higher stability of II.

It can be also observed that the trend of the Os-C vibration frequencies does not disagree with the $\nu(\text{C-N})$ trend, though such complementary behavior need not be expected in compounds of so low a symmetry.

A detailed analysis of the metal ground state and a tentative assignment of the d-d transitions are useful for clarifying the

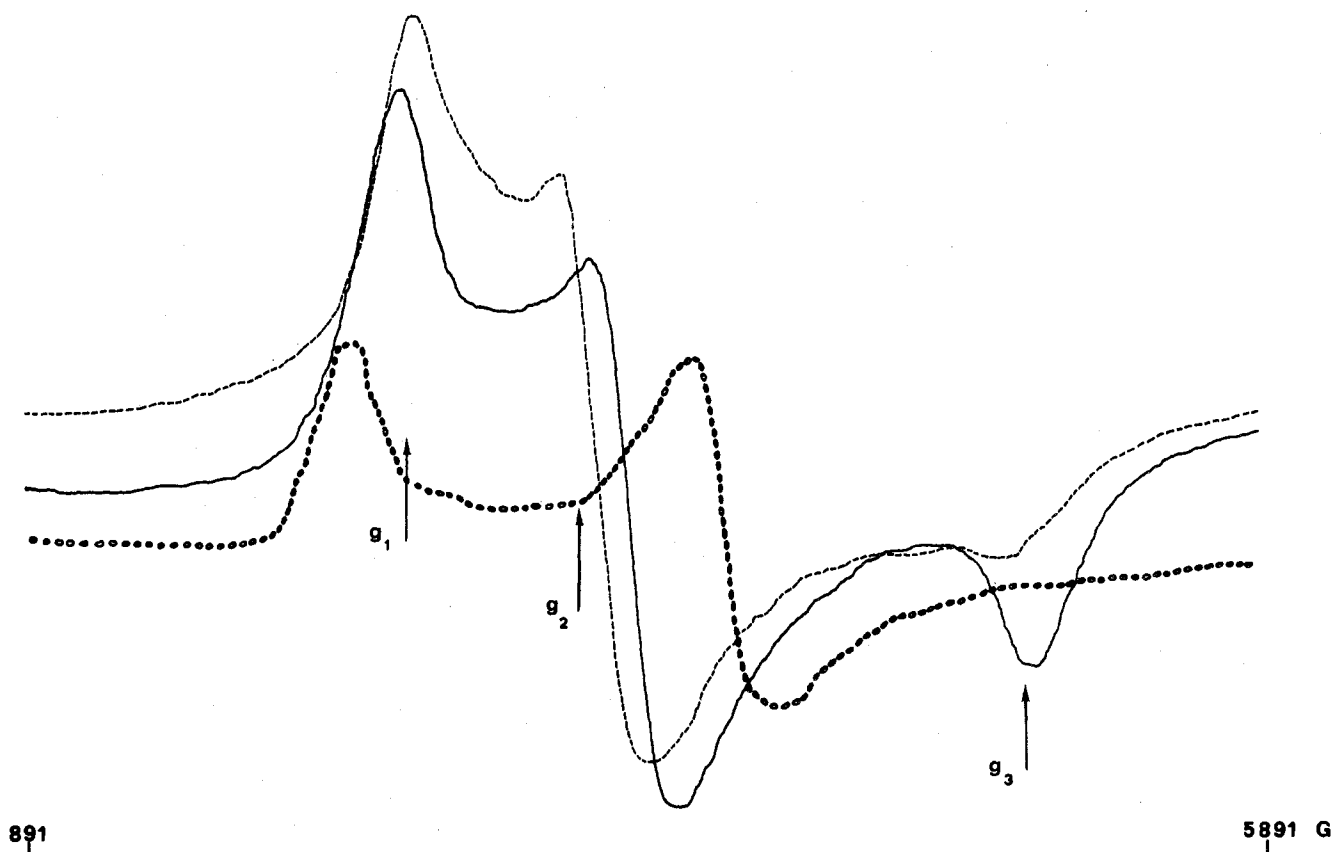


Figure 3. ESR spectra of $[\text{OsCl}_3(\text{AsPh}_3)_3]$ (OOO) and of $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$ in polycrystalline samples: isomer II (---); isomers I and III (—). $T = -170^\circ\text{C}$.

electronic properties of the complex $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$ and the perturbing influence of the isocyanide ligand on the electronic state of $[\text{OsCl}_3(\text{AsPh}_3)_3]$.

The calculations have been performed by applying the *hole formalism*, which considers the t_{2g}^5 configuration as a *one-hole* configuration. Perturbations due to spin-orbit coupling, low-symmetry field, and external magnetic field have been considered. The magnetic parameters, according to Griffith,⁹ assume the expressions

$$g_{xx} = 2[2AC - B^2 + kB(C - A)2^{1/2}]$$

$$g_{yy} = 2[2AC + B^2 + kB(C + A)2^{1/2}]$$

$$g_{zz} = 2[A^2 - B^2 + C^2 + k(A^2 - C^2)]$$

where A , B , and C are mixing coefficients for the components of the ground doublet state and the general expression of the ground state is assumed⁹ as

$$\psi^\pm = A|\pm 1^\pm\rangle \pm B|\zeta_1^\pm\rangle + C|\mp 1^\pm\rangle$$

The assignment of the ground-state configuration is clearly related to an unequivocal determination of the mixing coefficient values and to a sure assignment of the g components. The value of the Stevens constant k may be obtained from the coefficient normalization. In the absence of single-crystal analysis, the assignment of the principal g components shows 48 possible combinations, also depending on the sign of the experimental values. The choice has been carried out as follows.

(a) Forty-eight different assignments of g_1 , g_2 , and g_3 values have been considered and 48 different combinations of coefficients A , B , and C were obtained, together with an equal number of k values.

(b) The combinations which did not well reproduce the experimental g values or which gave k values much exceeding unity have been ruled out. In this way only 10 possible as-

signments can be considered, and they are clearly divided into two series of different k values ($k = 1.12$ and 0.8 for isomer II; $k = 1.09$ and 0.76 for isomers I and III).

(c) Knowledge of the coefficients A , B , and C , which are known functions of the spin-orbit coupling constant (λ), of the energy difference ($V = |E_{xz} - E_{yz}|$), and of the d_{xy} orbital energy (Δ) allows the diagonalization of the perturbation matrix and the determination of the energy levels of our system as a function of the spin-orbit coupling constant.^{1,9} The results of this calculation for the ten chosen combinations of g values have been examined, and only the combinations which reproduce both ν_1 and ν_2 electronic d-d absorptions for the same value of the spin-orbit coupling constant have been considered. In this way, only four assignments are available, which give $k = 0.8$ (isomer II) and $k = 0.76$ (isomers I and III). The value of the related spin-orbit coupling constant is $2500\text{--}2700\text{ cm}^{-1}$. The results of the calculations of the four most probable assignments of the magnetic tensors are reported in Table IV. As all assignments fit the experimental data, a definite choice of the g components is impossible on this basis.

(d) In comparing the d-orbital order associated, by V and Δ , with a possible assignment of the g components and the order derived from the field properties of the ligand molecules, self-consistency for isomer II is obtained on assigning g_1 to g_{yy} or g_{xx} , g_2 to g_{zz} , and g_3 to g_{xx} or g_{yy} with an orbital trend $xz > xy > yz$. This assignment also agrees with that proposed by Hudson and Kennedy for $[\text{OsX}_3\text{L}_3]$ complexes.¹ Isomers I and III have too low symmetries to be discussed in terms of d-orbital energy; however the great similarity of their electronic and magnetic properties suggests an analogous electronic ground configuration. By similar qualitative considerations, a d-orbital trend and a ground-state configuration analogous to that of the isocyanide derivatives can be assigned to $[\text{OsCl}_3(\text{AsPh}_3)_3]$, though the lack of the third resonance hinders detailed calculations.

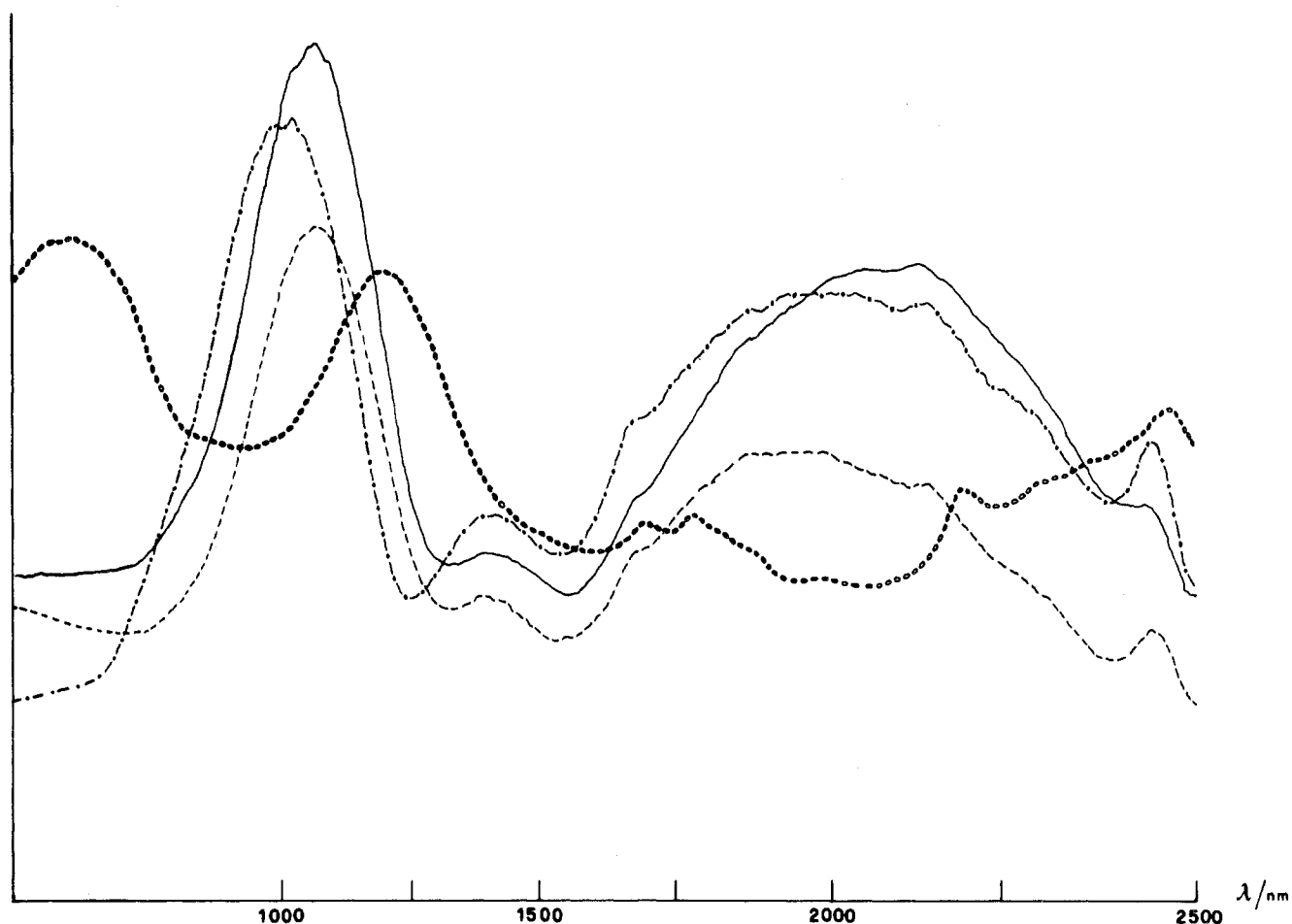


Figure 4. Diffuse reflectance electronic spectra of $[\text{OsCl}_3(\text{AsPh}_3)_3]$ (OOO) and of $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$: isomer II (---); isomer I (----); isomer III (—).

Table IV. Possible Assignment of the ESR Parameters and Related Electronic Energy Levels for $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$

	g_{xx}^a	g_{yy}^a	g_{zz}^a	k^b	V^c	Δ^c	ΔE_1^c	ΔE_2^c
Isomer II	1.4	2.79	2.13	0.8	3.54	0.11	1.87	3.90
	-2.79	-1.4	2.13	0.8	-3.54	0.11	1.87	3.90
	-2.13	-1.4	2.79	0.8	-1.66	-2.77	2.00	3.97
	1.4	2.13	2.79	0.8	1.66	-2.77	2.00	3.97
Isomers I and III	1.37	2.78	2.05	0.76	3.75	0.365	1.99	4.14
	-2.78	-1.37	2.05	0.76	-3.75	0.365	1.99	4.14
	-2.05	-1.37	2.78	0.76	-1.5	-3.14	2.35	4.19
	1.37	2.05	2.78	0.76	1.5	-3.14	2.35	4.19

^a Calculated values. ^b Stevens constant. ^c $|V| = |E_{xz} - E_{yz}|$; $\Delta = E_{xy}$; ΔE_1 and ΔE_2 are the calculated differences among three energy levels of the electronic system in spin-orbit coupling constant units.

The results in Table IV show that the energy differences between the three Kramers eigenstates are very similar to those between the one-hole functions d_{xy} , d_{xz} , and d_{yz} . So the most probable ground-state configuration of our complexes can be formulated as $(yz \text{ or } xz)^2(xy)^2(xz \text{ or } yz)$. The excited configurations, lying at ~ 5000 and $\sim 10000 \text{ cm}^{-1}$, are respectively $(yz \text{ or } xz)^2(xz \text{ or } yz)^2(xy)$ and $(xz \text{ or } yz)^2(xy)^2(yz \text{ or } xz)$. Therefore the electronic absorptions in the near-infrared region can be associated with the following electron transfers: $xy \rightarrow xz$ or yz (lower frequency); yz or $xz \rightarrow xz$ or yz (higher frequency). The third transition, which is visible only in the spectrum of $[\text{OsCl}_3(\text{AsPh}_3)_3]$ at $\sim 14000 \text{ cm}^{-1}$, can be tentatively assigned to the xz or $yz \rightarrow x^2 - y^2$ transition, though mixing with charge-transfer bands cannot be excluded.

A comparison between the mono-electronic levels of $[\text{OsCl}_3(\text{AsPh}_3)_3]$ and those of $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$ shows that the energy of the $d_{x^2-y^2}$ orbital is greatly increased by the presence of the isocyanide ligands in

the coordination sphere, so that the electron transfer $d_{xz \text{ or } yz} \rightarrow d_{x^2-y^2}$ shifts into the range obscured by the more intense charge-transfer bands. Moreover the substitution of two arsine by two isocyanide ligands increases slightly the splitting between the three d_π orbitals. This means a relevant contribution of the σ -bond type of interaction and is in accordance with the increase of the N-C bond energy, with respect to the free isocyanide ligand. The three isomers of $[\text{OsCl}_3(\text{AsPh}_3)(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_2]$ are very similar in their vibrational, electronic, and magnetic properties as a consequence of the low extent of $d_\pi - \pi^*$ overlap.

Conclusions

Upon considering the electronic perturbation of osmium(III) ion by coordination with isocyanide ligand, one can argue that this ligand provides a general approach toward octahedral symmetry, if the relative positions of the d_π orbitals are taken into account. The perturbation of the d_π osmium(III) orbitals,

smaller than the perturbation of the d_{σ} orbitals, shows that the isocyanide ligand is a relatively stronger π acceptor than the arsine ligand, as expected.

The electronic modifications of the isocyanide ligand, as seen in the variations in the C-N bond, are strongly related to the possibility of π -electron transfer from osmium to the isocyanide ligand. In isomers I and III, in which the isocyanide ligands are cis, the overlap $d_{\pi}-\pi^*$ is too small for the influence of the different electronic distributions to be transferred from the metal atom to the C-N group; in isomer II the two trans isocyanide ligands are clearly distinguishable.

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Registry No. Isomer I, 61491-27-8; isomer II, 61521-48-0; isomer III, 61521-49-1; *mer*-[OsCl₃(AsPh₃)₃], 61491-28-9; [OsCl₂-

(AsPh₃)₂(*p*-CH₃C₆H₄NC)₂], 61491-29-0.

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Complexes of the Platinum Metals. 8.^{1a} Electron Spectroscopy for Chemical Analysis Studies of Some Nitrosyl, Aryldiazo, and Aryldiimine Derivatives of Ruthenium, Osmium, Rhodium, and Iridium[†]

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ESCA spectra have been obtained for nitrosyl, aryldiazo, and aryldiimine complexes of ruthenium, osmium, rhodium, and iridium. The observed binding energies have been used, in conjunction with spectroscopic and structural data, to discuss the structures and electronic properties of the complexes investigated. A good correlation between the N 1s binding energies of the nitrosyl complexes and those of their aryldiazo analogues is found and lends further support to the view that nitrosyl and aryldiazo ligands possess similar coordination characteristics. The variation of metal binding energies with ligand substituents taken together with N 1s binding energies allows more reliable evaluation of ligand-metal bonding than N 1s binding energies alone. The values of the binding energies and the chemical shift difference for the N 1s electrons of the aryldiazo and aryldiimine ligands suggest that these moieties possess low overall charges and are appreciably less polar than dinitrogen ligands coordinated under similar circumstances.

Introduction

Extensive studies of the structural and electronic properties of transition metal nitrosyl complexes have led to the recognition of two limiting bonding modes involving linearly coordinated (NO⁺) or angularly bound (NO⁻) ligands.²⁻⁵ Experimentally observed systems approximate to one or the other of these two formal extremes. More recently, aryldiazo (N₂Ar) complexes have been tentatively assigned analogous structures containing linearly coordinated (N₂Ar⁺) or angularly bound (N₂Ar⁻) ligands, either on the basis of infrared data or by analogy with the corresponding nitrosyl derivatives.⁶ Partial confirmation of these assignments has been provided by x-ray diffraction studies on selected aryldiazo complexes⁶ including [RuCl₃(N₂Ar)(PPh₃)₂]solv (Ar = *p*-tolyl; solv = CH₂Cl₂⁷ or Me₂CO⁸) and [RhCl(N₂Ph){PhP(CH₂CH₂CH₂PPh₂)₂}] [PF₆]^{9,10} which reveal the presence of linearly coordinated (N₂Ar⁺) and angularly coordinated (N₂Ar⁻) ligands, respectively. Previous infrared^{7,11,12} and ESCA¹³⁻¹⁵ studies of metal nitrosyl complexes have shown that assignment of linear (NO⁺) or angular (NO⁻) geometries on the basis of nitrosyl infrared stretching frequencies [ν (NO)] and N 1s binding energies is not a valid procedure. The lack of a simple correlation between metal nitrosyl bonding modes

and spectroscopic parameters has been attributed to the fact that the energies of the metal d orbitals and the π^* orbitals of the NO ligand are similar. Under these circumstances the relative distribution of electrons between the metal and the nitrosyl ligand in the 2e molecular orbital can vary markedly within an isoelectronic series of complexes and relatively minor changes in the metal atom and/or other coordinated ligands may result in substantial differences in spectroscopic properties.¹⁶ Recently, however, an attempt has been made to establish a correlation between nitrosyl binding modes and ESCA data by employing the (O 1s-N 1s) binding energy difference as the ESCA parameter.¹⁷

In the present study nitrogen (N 1s) binding energies supplemented by metal binding energies have been employed to explore the formal analogy between nitrosyl and aryldiazo ligands and to seek a reliable correlation between ESCA data and NO or N₂Ar ligand bonding modes. Attempts to develop model systems for nitrogenase based on the reduction of coordinated dinitrogen or aryldiazo ligands has stimulated interest in the overall electronic charge and the polarity of these moieties and their reduction products.^{18,19} We have therefore measured N 1s electron binding energies for coordinated aryldiazo and aryldiimine ligands and compared our results with similar data previously reported for coordinated dinitrogen ligands.²⁰⁻²³ Finally, rather than use the NO⁺/NO⁻ notation

[†] No reprints of this paper are available from the authors.