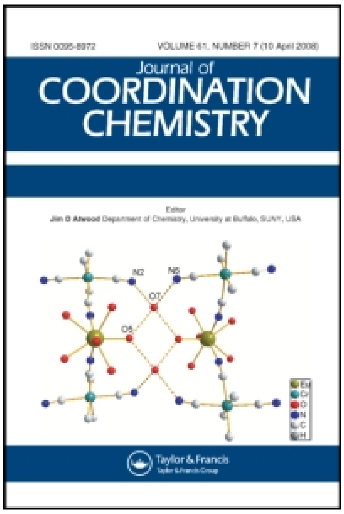

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THE JAHN-TELLER EFFECT IN A TRIGONAL BIPYRAMIDAL Ni(III) COMPLEX; SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF *trans*-NiI_3 $(PMe_3)_2$

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Reaction of $[Ni(\mu\text{-}t\text{-}Bu_2As)(PMe_3)_2]_2$, with I_2(Ni:I = 1:2) in toluene yields the black, crystalline Ni(III) complex *trans*-$NiI_3(PMe_3)_2$, (1), (38%). The coordination geometry about Ni is a distorted trigonal bipyramid with a distortion which can be attributed to a Jahn-Teller effect. One Ni-I bond (2.530(1)Å) is shorter than the other two (both 2.551(1)Å). Crystal data, (1), $C_6H_{18}I_3NiP_2$, M = 591.6, orthorhombic, space group *Pnma*, $a = 10.197(3)$, $b = 11.155(8)$ $c = 14.213(3)$Å, $U = 1616.7(5)$Å^3, $D_c = 2.43$ g cm^{-3}, $Z = 4$, $\lambda(MoK_\alpha) = 0.71073$ Å (graphite monochromator), $\mu(MoK_\alpha) = 70.4$ cm^{-1}. Refinement of 1168 reflection $I > 3\sigma(I)\}$ out of 1667 unique observed reflections ($2.0° < 2\theta < 50.0°$) gave R and R_w values of 0.046 and 0.066, respectively. The Ni-P distances are 2.246(2) Å and 2.253(2) Å.

Keywords: X-ray, nickel, iodide, phosphine, complex.

INTRODUCTION

There are very few complexes of Ni(II), and most of them are kinetically unstable.[1] Some apparent Ni(III) complexes can be more accurately described as Ni(II) complexes in which a ligand has been oxidized, as in the case of $[Ni(diars)_2Cl_2]^+$ {diars = $o\text{-}C_6H_4(AsMe_2)_2$}. The X-ray crystal structure determination of this complex showed the nickel atom in a nearly octahedral environment.[2] The genuinely Ni(III) complex K_3NiF_6 has a distorted octahedral geometry with one axis elongated as a result of the Jahn-Teller effect arising from a $t_{2g}^6e_g^1$ electronic configuration.[3] The first Ni(III) complex, $NiBr_3(PEt_3)_2$, was prepared by Jensen[4] in 1936. A similar complex, $NiBr_3(PMe_2Ph)_2$ was synthesized by Alyea and Meek[5] by the reaction of $NiBr_2(PMe_2Ph)_2$ with bromine in benzene, and a crystal structure determination was carried out by Stalick and Ibers.[6] The complex was found to have a distorted trigonal bipyramidal geometry, with axial phosphines and three equatorial bromine atoms. One of the Ni-Br bonds (Ni-Br = 2.375(2)Å) was significantly longer than the other two (2.339(2) Å and 2.349(2)Å) and the Br-Ni-Br angle for the latter two bromines was 132.7° which is considerably greater than the idealized angle of 120°.

We report here the preparation and X-ray crystal structure of *trans*-$NiI_3(PMe_3)_2$, (1), which can be isolated from the reaction of $[Ni(\mu\text{-}t\text{-}Bu_2As)(PMe_3)]_2$[7] with iodine at room temperature. (1) also displays a Jahn-Teller distortion which is, however, the converse of that exhibited by $NiBr_3(PMe_2P)_2$, *i.e.*, it has one Ni-I bond which is significantly shorter than the other two and one I-Ni-I angle significantly less than the idealized angle of 120°.

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EXPERIMENTAL

All operations were performed under oxygen free nitrogen or under vacuum. Toluene was distilled from sodium metal under nitrogen before use. Instruments: IR, Perkin-Elmer 1330; ESR, Varian E-9. $[Ni(\mu\text{-}t\text{-}Bu_2As)(PMe_3)]_2$ was prepared as previously described.[7]

Preparation of trans-NiI$_3$(PMe$_3$)$_2$, (1).

A solution of $[Ni(\mu\text{-}t\text{-}Bu_2As)(PMe_3)]_2$ (0.32 g, 0.49 mmol) in toluene (20 cm^3) was cooled to -78°C and a solution of iodine (0.278 g, 1.1 mmol) in toluene (10 cm^3 was added slowly. After 1.5 h, the black reaction mixture was allowed to warm to room temperature and was stirred for an additional 12 h. The solution volume was reduced to *ca* 10 cm^3 by evaporation under vacuum at room temperature, and cooling (-5°C) resulted in the formation of flat, black plates of $NiI_3(PMe_3)_2$, (1). They were isolated and dried under vacuum. Yield 0.11 g (38%), M.P. 85-87°C (dec.), ESR ambient temperature, C_6D_6, 5 mm glass tube), $v = 9.370$ GHz, power = 150 mW, $g = 2.063$, (single broad absorption, no hyperfine coupling observed). IR(KBr disc) 1390 m, 1265 m, 920 s, 785 w, 720 w, (cm^{-1}).

X-Ray Experimental

Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated MoK_α radiation. Data were collected by the $\theta/2\theta$ scan technique at 23 ± 2°C. Details of the standard data collection methods are as described in ref. 8. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP-PLUS. A crystal of (1) was mounted in a thin-walled glass capillary tube under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 24.0° and 26.0°. Systematic absences indicated a choice of either *Pnma* or $Pna2_1$ as the space group. *Pnma* was chosen on the basis of successful refinement. Details of crystal data parameters and other relevant information are collected in Table I. Key bond lengths and angles are in Table II and positional parameters in Table III. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was made using a psi scan method (Program EAC). The coordinates of the Ni atom were obtained by direct methods (MULTAN).[9] and the remaining non-hydrogen atoms were located by successive cycles of least-squares refinement followed by difference Fourier maps. A non-Poisson contribution weighting scheme was used in the least-squares refinement with an experimental instability factor *P* of 0.03.[10] All heavy atoms were refined anisotropically, and hydrogen atoms were not located. The highest peak in the final difference Fourier was 1.58 e Å^{-3}. Tables of thermal parameters and structure factors have been deposited with the Editor-in-Chief, and are available on request.

RESULTS AND DISCUSSION

The reaction of $[Ni(\mu\text{-}t\text{-}Bu_2As)(PMe_3)]_2$ with iodine in toluene at room temperature proceeds smoothly and results in the fragmentation of the dimer to give $NiI_3(PMe_3)_2$ (38%). There are other products present in the reaction mixture although we have been unable to isolate or identify them fully.

TABLE I
Crystal Structure Parameters for *trans*-$NiI_3(PMe_3)_2$.

Description of Crystal	(1)
Color	black
Habit	plate
Maximum crystal dimensions (mm)	0.15 x 0.35 x 0.70
Unit Cell	
Crystal system	orthorhombic
Space group	*Pnma* (No. 62)
Unit cell parameters:	
a(Å)	10.197(3)
b(Å)	11.155(8)
c(Å)	14.213(3)
Unit cell volume (Å^3)	1616.7(5)
Molecules per unit cell	4
Formula	$C_6H_{18}I_3NiP_2$
Molecular weight (g mol^{-1})	591.6
Density (calc. g cm^{-3})	2.43
μ(calc) (cm^{-1})	70.4
Data Collection	
Radiation (Å)	MoK_α, (0.71073)
Scan technique	$\theta/2\theta$
Scan width (deg.)	0.8 + 0.35 tan θ
Range of indices	$+h, +k, +l$
2θ range (deg.)	2–50
No. reflections measured	1667
intensity	*0 6 4, 2 3 7*
orientation	*3 4 5, 4 5 0*
Decay of standards	-0.5%
Minimum % transmission	38%
Maximum % transmission	99%
Average % transmission	73%
Structure Determination	
No. reflections used ($I > 3\sigma(I)$)	1168
No. parameters varied	82
Data/parameter ratio	14.2
Shift to error ratio	0.074
E.s.d. of an observation of unit weight	11.03
R	0.046
R_w	0.066

TABLE II
Bond Distances (Å) and Angles (°) for $NiI_3(PMe_3)_2$.

Distances

Atom 1	Atom 2	Distance[a]	Atom 1	Atom 2	Distance
I1	Ni	2.551(1)	Ni	P2	2.253(2)
I2	Ni	2.530(1)	P1	C10	1.801(3)
Ni	P1	2.246(2)	P1	C11	1.868(5)
P2	C20	1.826(10)	P2	C21	1.844(5)

Angles

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Ni	P1	C10	114.1(3)	I1	Ni	I1′	114.70(4)
Ni	P1	C11	115.4(2)	I1	Ni	I2	122.65(2)
C10	P1	C11	103.8(3)	I1	Ni	P1	89.93(4)
C11	P1	C11′	102.8(4)	I1	Ni	P2	90.35(4)
Ni	P2	C20	114.6(3)	I2	Ni	P1	89.37(6)
Ni	P2	C21	114.2(2)	I2	Ni	P2	90.09(6)
C20	P2	C21	104.5(3)	P1	Ni	P2	179.47(9)
C21	P2	C21′	103.6(4)				

[a] Numbers in parentheses are estimated standard deviations.

TABLE III

Positional Parameters and their Estimated Standard Deviations for $NiI_3(PMe_3)_2$.

Atom	*x/a*	*y/b*	*z/c*	*B*(Å²)
I1	0.7845(1)	0.0575(1)	0.09955(8)	4.25(2)
I2	0.5338(2)	0.250	−0.1083(1)	5.32(4)
Ni	0.6970(3)	0.250	0.0258(2)	2.89(5)
P1	0.5296(7)	0.250	0.1284(4)	3.5(1)
P2	0.8637(7)	0.250	−0.0783(4)	3.8(1)
C10	0.579(3)	0.250	0.250(2)	4.5(6)
C11	0.416(2)	0.381(2)	0.120(1)	5.2(4)
C20	1.027(3)	0.250	−0.025(2)	5.6(7)
C21	0.865(2)	0.380(2)	−0.158(1)	5.9(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as

$(4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\alpha).B(1,2) + ac(\cos\beta).B(1,3) + bc(\cos\alpha).B(2,3)]$

Trans-$NiI_3(PMe_3)_2$, (1), crystallizes in the orthorhombic space group *Pnma* with half a molecule in the asymmetric unit (four per unit cell). The molecule lies on a crystallographic mirror plane which passes through Ni, I(2), P(1), P(2), C(10), and C(20) (Figure 1). The coordination geometry about Ni is trigonal bipyramidal; however, the molecule has a distortion that is the converse of that exhibited by the bromine complex $NiBr_3(PMe_2Ph)_2$, presumably the result of a Jahn-Teller effect. Thus, (1) has one Ni-I bond that is significantly shorter than the other two {Ni-I(2) = 2.530(1) Å and Ni-I(1) = Ni-I(1′) = 2.551(1) Å}. The I(1)-Ni-I(1′) angle of 114.80(4)° is less than the idealized angle of 120°.

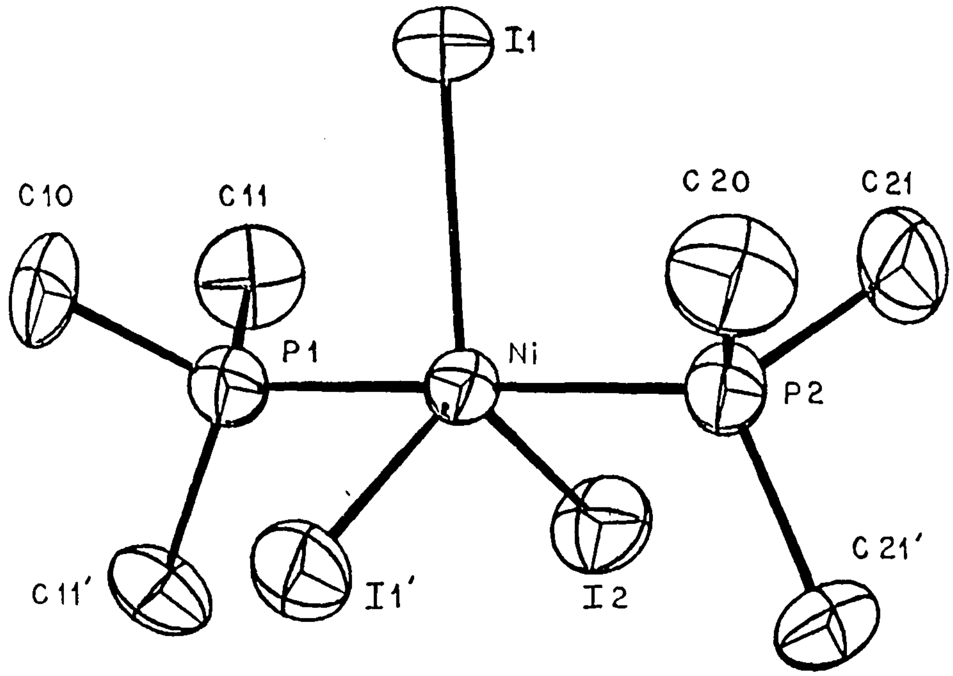
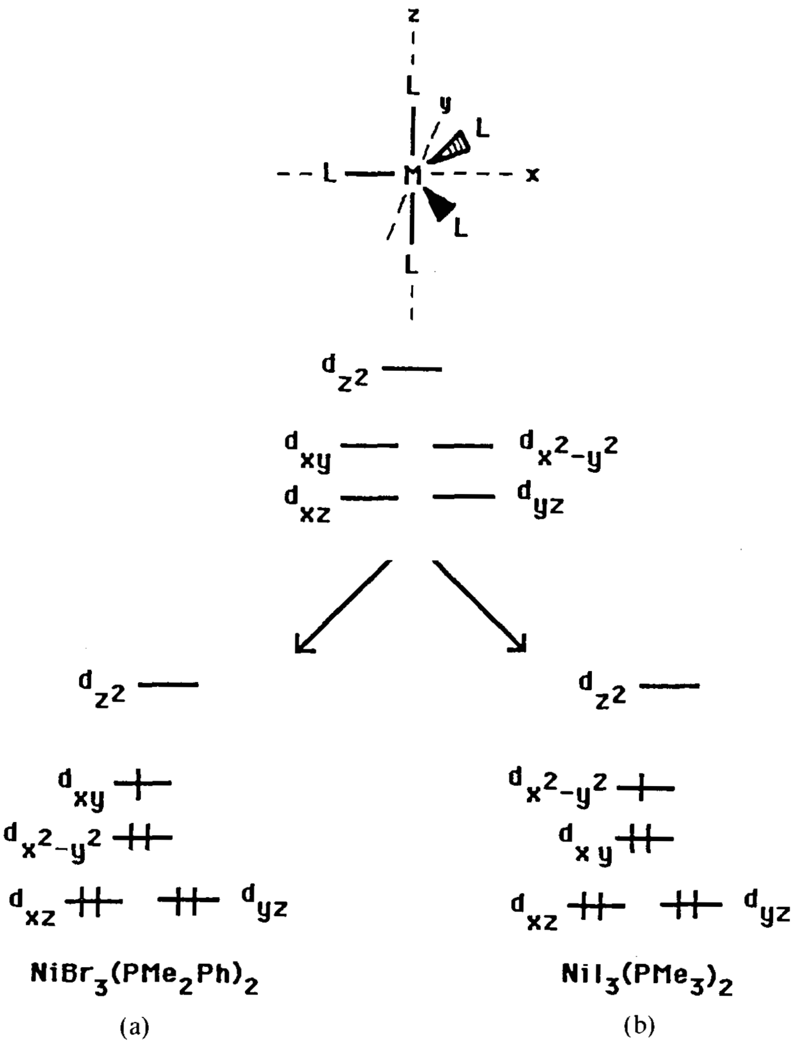


FIGURE 1 Ortep view of *trans*-$NiI_3(PMe_3)_2$.

Scheme I



Assuming no steric effects, thse deviations can be explained in terms of d-orbital occupancy for low spin Ni(III). A trigonal bipyramidal arrangement of ligands splits the metal d-orbitals into three sets as shown in Scheme I. The degeneracy is lowered further since three electrons would occupy the two degenerate d_{xy} and $d_{x^2-y^2}$ orbitals. The arrangement with one electron in the $d_{x^2-y^2}$ and two in the d_{xy} orbital allows for fewer metal-ligand electronic repulsions for one ligand relative to the other two. This results in one shorter metal ligand bond and a smaller X-M-X angle (X = Br, I) between the other two equatorial groups because of ligand-ligand repulsions. Conversely, if there are two electrons in the $d_{x^2-y^2}$ and one electron in the d_{xy} orbital, then one of the equatorial metal-ligand bonds will be longer than the other two and the L-M-L angle opposite the long bond will be greater than 120°. Clearly, situation (a) of the scheme applies to $NiBr_3(PMe_2Ph)_2$ and (b) applies to $NiI_3(PMe_3)_2$.

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