Synthesis and Crystal Structure of Tetrakis(2-pyridinecarboxylato)niobium(IV)−2-Ethanol, an Octacoordinate Dodecahedral d^1 $M(A\text{-}B)_4$ System

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Introduction

Various aspects of octacoordination in transition metal complexes have been extensively reviewed.[1−3] Factors which govern the stereochemistry of octacoordinate complexes have been the subject of various papers,[4−10] and the geometries which are prevalent are the D_{2d} dodecahedron or the D_{4d} square antiprism. Theoretical studies on simple MA_8 systems have shown that both the D_{2d} and D_{4d} stereochemistries are equally likely on the basis of crystal field stabilization or minimization of ligand−ligand repulsive forces.[2] The MA_8 and MA_4B_4 systems are dominated by dodecahedral structures. With chelating bidentate ligands, the $M(A\text{-}A)_4$ systems are divided between dodecahedral and square antiprism geometries, while for the $M(A\text{-}B)_4$ systems the stereochemistry is predominantly dodecahedral.

Besides the stereochemistry, the nature of bonding is a topic which has received much attention. A stereochemical rule applying to the geometries of transition metal octacoordinate complexes proposed by Orgel in 1960[11] suggested a dodecahedral stereochemistry for octacoordinate systems of the type MA_4B_4. For d^1 and d^2 metal ions where A is π-nonbonding or a π-donor and B is a π-acceptor, the π-acceptor B ligands form a flattened tetrahedral array near the d_{xy} orbital and diagonal to the occupied $d_{x^2-y^2}$ orbital while the positions beyond the d_{xz}−d_{yz} maxima toward the z-axis are occupied by the A ligands. Further extension of Orgel's ideas suggests that d^1 and d^2 dodecahedral $M(A\text{-}B)_4$ molecules are expected to have such structures, whereas in the d^0 $M(A\text{-}B)_4$ complexes the ligands are sorted out in the reverse order with the π-donor ligands accommodated at B sites while π-acceptor ligands occupy the A sites. The X-ray crystal structures of $[W(Brquin)_4]$ (Brquin = 5-bromoquinolin-8-olate)[12] and $[Zr(quin)_4]$ (quin = quinolin-8-olate)[13] have provided the evidence for Orgel's postulate in the case of d^2 and d^0 configurations, respectively.

Table 1. Crystallographic Data for $[Nb(pyc)_4]\cdot 2C_2H_5OH$

molecular formula	$C_{28}H_{28}N_4O_{10}Nb$
fw	673.46
cryst color, habit	red-purple, cubic
space group	$P2_1/a$
a, Å	15.524(4)
b, Å	11.981(3)
c, Å	15.353(4)
β, deg	92.19(2)
V, Å^3	2853(1)
Z	4
D_{calc}, gcm^{-3}	1.568
D_{obsd}, gcm^{-3}	1.57
λ, Å	0.710 69
abs coeff, μ, cm^{-1}	4.9
R^a	0.032
$R_w{}^b$	0.046

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

To further consolidate Orgel's postulate on the control of stereochemistry of octacoordinate complexes by the electronic configuration of the transition metal ion, we report here the X-ray crystal structure of the complex $[Nb(pyc)_4]\cdot 2C_2H_5OH$ (pyc = 2-pyridinecarboxylate).

Experimental Section

Starting Materials. Commercial reagent grade chemicals niobium pentachloride, 2-pyridinecarboxylic acid, and zinc powder from Merck were used without further purification.

Preparation of $Nb(pyc)_4$. All manipulations were carried out under an argon or nitrogen atmosphere. Niobium pentachloride (0.50 g, 1.85 mmol) was added to Zn powder (0.24 g, 3.7 mmol), followed by 20 cm^3 of absolute ethanol, and left to stir at room temperature for 3 h. The reaction mixture turned green immediately and darkened gradually to dark brown. 2-Pyridinecarboxylic acid (0.91 g, 7.4 mmol) dissolved in 50 cm^3 of ethanol was then added to the reaction mixture. A dark red-purple color was formed along with some dark brown precipitate. Stirring was continued for 30 min after which the brown solid was filtered off and the filtrate was left at 4 °C. Dark red-purple crystals of X-ray quality were obtained overnight. The crystals were isolated by suction filtration, washed with a small amount of cold ethanol and then dried under a stream of argon. A second crop of crystals can be obtained by evaporation of the solvent. Yield: 70% based on niobium pentachloride. Anal. Calcd for $C_{24}H_{16}N_4O_8Nb$: C, 49.58; H, 2.75; N, 9.64; Nb, 15.99. Found: C, 48.98; H, 2.73; N, 9.38; Nb, 16.08.

Physical Measurements. UV−visible spectra of ethanolic solutions were recorded on Hewlett-Packard 8452A diode-array spectrophotometer. IR spectra were recorded as KBr pellets on a Perkin-Elmer FT1600 spectrometer. Magnetic susceptibility measurements were carried out using the Johnson Matthey Catalytic System Division magnetic susceptibility balance.

X-ray Crystal Structure Determination. Crystallographic data are summarized in Table 1. A red-purple cubic crystal of approximate dimensions 0.24 × 0.24 × 0.24 mm was mounted in a glass capillary with mother liquor and set on a MacScience MXC-18 diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 69 Å) was used. Data were collected at a temperature of 293 ± 1K using the $\omega-2\theta$ scan technique. The structure was solved by and expanded using Fourier techniques (DIRDIF92).[14] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were included in fixed positions. A total of 6689 reflections with $I > 1.50\sigma(I)$ were used in the refinement (full-matrix least squares). All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corp. (1985 and 1992).

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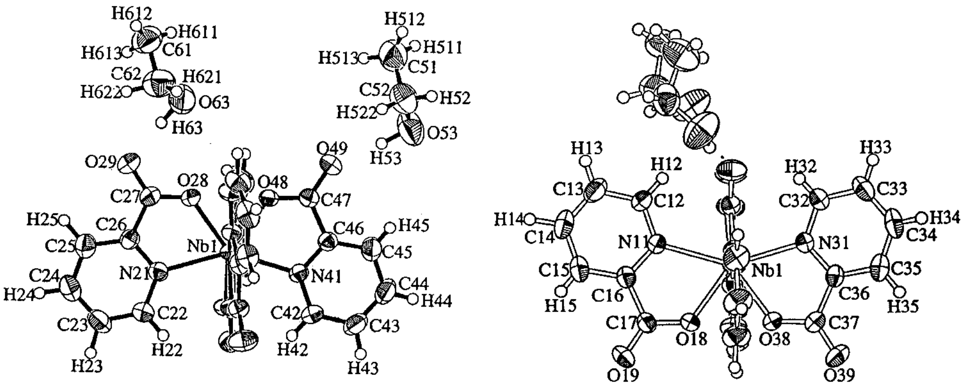

Figure 1. View of the $[Nb(pyc)_4]\cdot 2C_2H_5OH$ molecule along the ABBA trapezoidal planes, with the planes defined by the donor atoms of ligands 1 and 3 (for the structure on the right) and ligands 2 and 4 (for the structure on the left).

Table 2. Bond Distances (Å) and Angles (deg) Defining the Coordination Polyhedron of $[Nb(pyc)_4]$, with Parameters Listed According to Hoard−Silverton Nomenclature[4]

	Distances r_a		
Nb−O18	2.099(2)	Nb−O38	2.092(2)
Nb−O28	2.096(1)	Nb−O48	2.108(1)
	Distances r_b		
Nb−N11	2.295(2)	Nb−N31	2.296(2)
Nb−N21	2.310(2)	Nb−N41	2.307(2)
	Distances *a*		
O18−O38	2.456(2)	O28−O48	2.456(2)
	Distances *b*		
N11−N21	3.344(3)	N31−N41	3.163(3)
N21−N31	3.527(3)	N41−N11	3.445(3)
	Distances *g*		
N11−O28	2.784(2)	N31−O28	2.790(2)
N11−O48	2.697(2)	N31−O48	2.720(2)
N21−O18	2.789(2)	N41−O18	2.768(2)
N21−O38	2.725(3)	N41−O38	2.764(2)
	Distances *m*		
N11−O18	2.528(2)	N38−O38	2.529(2)
N21−O28	2.531(2)	N41−O48	2.533(2)
	Angles O−Nb−O		
O18−Nb−O38	71.74(5)	O28−Nb−O48	71.49(6)
	Angles N−Nb−N		
N11−Nb−N31	147.99(6)	N21−Nb−N31	99.94(6)
N21−Nb−N41	148.94(7)	N31−Nb−N41	86.79(6)
N11−Nb−N21	93.12(6)	N41−Nb−N11	96.92(6)
	Angles N−Nb−O		
N11−Nb−O18	70.08(6)	N31−Nb−O38	70.20(6)
N21−Nb−O28	69.91(6)	N41−Nb−O48	69.86(6)

Selected bond distances and angles are listed in Table 2, while the rest of the crystallographic data have been submitted as Supporting Information.

Results and Discussion

Synthesis and Properties. A convenient method has been sought for the entry into the coordination chemistry of niobium. The zinc reduction of ethanolic solutions of niobium pentachloride provides a convenient and efficient route to medium-valent niobium compounds. In the present study, reaction of 2-pyridinecarboxylic acid with zinc-reduced niobium pentachloride in ethanol affords $[Nb(pyc)_4]$ in good yield.

The $[Nb(pyc)_4]$ complex is stable under inert atmosphere but is oxidized slowly in air to a white product. In the IR spectrum, the shift of −C═O stretching to 1680 from 1700 cm^{-1} for the free ligand, as well as the absence of the characteristic double band of pyridine ring in the 1600 cm^{-1} region, supports the coordination of both carboxylato O and pyridinato N to niobium. In the UV−visible spectrum, the complex exhibits charge transfer bands at 228 nm (ϵ = 20 270 M^{-1} cm^{-1}) and 266 nm (ϵ = 21 000 M^{-1} cm^{-1}) and d−d transition(s) appears as an unsymmetrical band at 508 nm (ϵ = 3970 M^{-1} cm^{-1}) with a slight shoulder at 450 nm (ϵ = 2500 M^{-1} cm^{-1}). The rather high extinction coefficient associated with the d−d transition(s), which probably gained intensity from charge transfer, has previously been reported for other octacoordinate Nb(IV) complexes.[15]

Table 3. Weighted Least-Squares Trapezoidal ABBA Planes

atoms	*x*	*y*	*z*
Nb1	0.22210(1)	0.01108(1)	−0.23086(1)
O18	0.18344(9)	−0.1568(1)	−0.2350(1)
O28	0.30218(9)	0.1038(1)	−0.14499(9)
O38	0.08732(9)	0.0061(1)	−0.2398(1)
O48	0.31683(9)	0.0910(1)	−0.30338(9)
N11	0.3405(1)	−0.1030(1)	−0.2166(1)
N21	0.1835(1)	−0.0185(1)	−0.0889(1)
N31	0.1685(1)	0.1880(1)	−0.2525(1)
N41	0.1949(1)	−0.0176(1)	−0.3780(1)

Least-Squares Plane No. 1

atoms defining plane	dist (Å)	esd
Nb1	−0.0020	0.0002
O18	0.1113	0.0016
O38	−0.0632	0.0017
N11	0.0303	0.0017
N31	0.1357	0.0017

mean deviation from plane 0.0685 Å; χ^2 = 12387.0

Least-Squares Plane No. 2

atoms defining plane	dist (Å)	esd
Nb1	0.0005	0.0002
O28	−0.0821	0.0015
O48	0.0598	0.0014
N21	0.0301	0.0018
N41	−0.0845	0.0018

mean deviation from plane 0.0514 Å; χ^2 = 7410.4

Dihedral Angles between Least-Squares Planes

plane	plane	angle (deg)
2	1	88.26

The magnetic susceptibility is 1.44 μ_B at 298 K, which conforms to a Nb(IV) having a $4d^1$ configuration. As can be expected for a second-row transition element, this value is lower than the spin-only value and is consistent with the magnetic susceptibility of the octacoordinate tetrakis(acetylacetonato)niobium(IV).[15] This value is however higher than the magnetic

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moments of approximately 1.3 μ_B for six-coordinate Nb(IV) compounds.[16−18]

Structure of $[Nb(pyc)_4]\cdot 2C_2H_5OH$. The X-ray crystallographic study on the crystal of the complex in the mother liquor reveals units of $[Nb(pyc)_4]$ which are hydrogen-bonded to two molecules of ethanol per unit complex. A dodecahedral geometry is adopted by the Nb(IV) atom with the bidentate 2-pyridinecarboxylato ligands spanning the *m* edges of a dodecahedron to give a D_{2d} *mmmm* stereoisomer. The shape of the dodecahedron is described by the parameters in Table 2. An ORTEP drawing of the $[Nb(pyc)_4]\cdot 2C_2H_5OH$ molecule along the two different ABBA trapezoidal planes is shown in Figure 1. The interpenetrating ABBA trapezoids are nearly perpendicular, with a dihedral angle of 88.26° between the weighted least-squares planes (Table 3). The metal atom and the atoms which define the individual trapezoid are planar to within 0.14 Å. This is in agreement with the D_{2d} dodecahedral geometry where these planes are perpendicular, whereas the angle between corresponding planes in the idealized D_{4d} square-antiprism is 77.4°.[9]

Of particular interest is the occupancy of the Hoard−Silverton designated A,B coordination sites. The four π-acceptor pyridinato N atoms occupy the B sites and lie 2.295−2.310 Å (Table 2) from the niobium center, while the π-donor carboxylato oxygens occupy the A sites at distances of 2.092−2.108 Å. This pattern of A,B site occupancy in the d^1 $[Nb(pyc)_4]$ complex is also displayed by the d^2 $[W(Brquin)_4]$ complex.

The role of π-bonding is believed to be important in determining the occupancy of the A,B sites. In the dodecahedron, the $d_{x^2-y^2}$ orbital can π-bond specifically to the ligand atoms of the B type only since it lies in the *xy* plane. In d^1 and d^2 metal complexes, metal → ligand π-bonding can occur; hence, it is predicted that the π-acceptor ligands occupy the B sites. However, in the case of d^0 metal complexes only ligand → metal π-bonding can occur so the B sites would be occupied by π-donor ligands.

The validity of this conclusion is indeed demonstrated by this work on the d^1 metal complex $[Nb(pyc)_4]$, along with the previously reported work on d^2 $[W(Brquin)_4]$ and d^0 $[Zr(quin)_4]$. In the absence of severe steric interactions, the stereochemistry of octacoordinate dodecahedral complexes is controlled by the electronic configuration and π-bonding (whether metal → ligand or ligand → metal).

Conclusion

The $[Nb(pyc)_4]$ complex provides the first experimental evidence for Orgel's postulate regarding octacoordinate d^1 $M(A\text{-}B)_4$ stereochemistry whereby the π-acceptor ligand is predicted to occupy the B sites and the π-donor ligands occupy the A sites of the dodecahedron.

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Supporting Information Available: Atomic coordinates (Table S1), anisotropic displacement parameters (Table S2), bond lengths (Table S3), bond angles (Table S4), and nonbonded angles (Table S5) (13 pages). Ordering information is given on any current masthead page.

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