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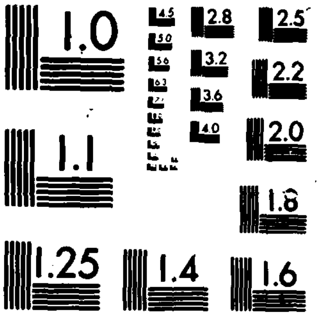

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The primary purpose of this investigation was to gain a better understanding of the fundamental chemistry of the early transition elements in their high oxidation states. The work involved the preparation and characterization of titanium, zirconium and hafnium poly(prazolyl)borate complexes with emphasis on the structure, mode of bonding and magnetic behavior of these complexes.

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THE STUDY OF SOME EARLY TRANSITION METALS IN OXIDATION STATE IV USING THE POTASSIUM POLY(PYRAZOLYL)BORATES AS LIGANDS

FINAL REPORT

BOBBY L. WILSON

OCTOBER 11, 1985

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STATEMENT OF PROBLEM

The primary purpose of this investigation was to gain a better understanding of the fundamental chemistry of the early transition elements in their high oxidation states. The work involved the preparation and characterization of titanium, zirconium and hafnium poly(prazolyl)borate complexes with emphasis on the structure, mode of bonding and magnetic behavior of these complexes.

TETRAKIS(PYRAZOLYL)BORATE COMPLEXES

The reactions of zirconium tetrahalides, $ZrCl_4$, $ZrBr_4$ and ZrI_4, and hafnium tetrahalides, $HfCl_4$ and HfI_4, with stoichiometric amounts of potassium tetrakis-(pyrazolyl)borate, $K(B(Pz)_4)$ in dichloromethane or toluene proceeded according to equation I.

$$MX_4 + 4K(B(Pz)_4) \rightarrow M(B(Pz)_4)_4 + 4KX \qquad (I)$$

The products were isolated as white powders which were quite soluble in dicholormethane and toluene.

Proton magnetic resonance spectra of the complexes were recorded at ambient temperature using CD_2Cl_2 as solvent and $SiMe_4$ as an internal standard. The spectrum of each complex exhibited three resonanaces (singlet, doublet and triplet). The observation of only three resonances is an indication that the fully substituted complexes are stereochemically nonrigid. This fluxional behavior was attributed to a tumbling or exchange process.

When two moles of the potassium tetrakis(pyrazolyl)borate were allowed to react with one mole of ZrI_4, $HfCl_4$ or HfI_4 the reactions occurred according to equation II.

$$MX_4 + 2K(B(Pz)_4) \rightarrow MX_2(B(Pz)_4)_2 + 2KX \qquad (II)$$

Products were isolated as brownish-red, light orange and yellow crystalline solids for the ZrI_4, $HfCl_4$ and HfI_4 respectively. The complexes were air and water sensitive as indicated by color changes when exposed to the atmosphere or placed in water.

The 'H nmr and ^{13}C nmr spectrum of the zirconium complex each consisted of six and seven resonances respectively that implied a tridentate nature of the $B(Pz)_4^-$ ligand and therefore eight coordination around zirconium. The spectrum of each hafnium complex exhibited only three resonances. The observation of only three resonances corresponded to four equivalent pyrazolyl groups which was attributed to a tumbling or exchange process.

HYDROTRIS(PYRAZOLYL)BORATE COMPLEXES

The reactions of zirconium tetrahalides (Cl and Br) with 1:2 molar amounts of potassium hydrotris(pyrazolyl)borate, $K(HB(Pz)_3)$, in dichloromethane proceeded according to the equation III.

$$ZrX_4 + 2K(HB(Pz)_3) \rightarrow ZrX_2(HB(Pz)_3)_2 + 2KX \qquad (III)$$

The $ZrCl_2(HB(Pz)_3)_2$ complex was isolated as flaky white crystals which were extremely soluble in dichloromethane. $ZrCl_2(HB(Pz)_3)_2$ also showed good solubility in chloroform, dimethylformamide, dimethylsulfoxide and was insoluble in benzene and tetrahydrofuran. $ZrBr_2(HB(Pz)_3)_2$ was isolated as flaky crystals with a pinkish tint. The infrared spectra of both the chloride and bromide complexes were virtually identical with the B-H and aromatic C-H bonds at 2500 cm^{-1} and 3110 cm^{-1} respectively. The 'H nmr spectra were obtained using deuterated chloroform as solvent. The present of two sets of triplets and doublets for each complex suggested a bidentate nature of the ligand with the formation of eight-coordinate complexes.

White crystalline dichlorbis (hydrotris(pyrazolyl)borate) hafnium (IV) was obtained by the reaction of a 1:2 molar ratio of hafnium tetrachloride with potassium hydrotris(pyrazolyl)borate. The reaction proceeded according to equation IV.

$$HfCl_4 + 2K(HB(Pz)_3) \rightarrow HfCl_2(HB(Pz)_3)_2 + 2KCl \qquad (IV)$$

An eight-coordinate structure was assigned based on the 'H nmr and the infrared spectra.

Tetrakis (hydrotris(pyrazolyl)borate) hafnium (IV) was prepared according to reaction V.

$$HfCl_4 + 4K(HB(Pz)_3) \rightarrow Hf(HB(Pz)_3)_4 + 4KCl \qquad (V)$$

The complex was recovered as a white crystalline powder with a melting point range of 58° to 60°C. The 'H nmr spectrum showed only a triplet at δ6.6 and a doublet at δ8.0. The observation of only two peaks implied spectroscopic identify of the three pyrazolyl gfoups and a tumbling process was suggested to explain this spectroscopic identity.

Samples of these and other compounds are available for testing of catalytic characteristics in advanced propellant application.

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