

Unusual Tetragonality in Dibromotetrapyrazolenickel(II)

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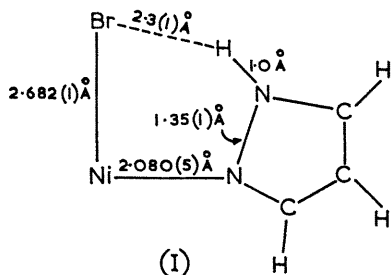
(Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234)

In the visible spectrum of $\text{Ni py}_4\text{Br}_2$ ($\text{py} = \text{pyridine}$), the two lowest energy bands are separated by *ca.* 3000 cm^{-1} .¹ Although this separation indicates a substantial tetragonal distortion from the octahedral field present in the parent Ni py_6^{2+} species, Rowley and Drago further showed that the magnitude of the observed tetragonal splitting is consistent with that computed by using typical spectrochemical series values of the ligand-field strength parameters, Dq , for pyridine and for the bromide ion. We have determined the structures of the two pyrazole (pz) complexes, $\text{Ni pz}_6(\text{NO}_3)_2$ (R 0.053 for 1115 reflections),² and $\text{Ni pz}_4\text{Br}_2$ (R 0.081 for 2104 reflections).³ The bromide complex is a *trans*-substituted species of the octahedral Ni pz_6^{2+} cation which is shown to be present in the structure of $\text{Ni pz}_6(\text{NO}_3)_2$. Therefore, the spectra of these pyrazole complexes can be compared with those of the analogous pyridine complexes. As expected, the crystal spectrum of $\text{Ni pz}_6(\text{NO}_3)_2$ is similar to that of Ni py_6^{2+} , hence Dq -(pyrazole) and Dq -(pyridine) are similar. However, the tetragonal splitting between the first two bands in the spectrum of $\text{Ni pz}_4\text{Br}_2$ is found to be *ca.* 1000 cm^{-1} larger than the corresponding splitting observed in the spectrum of $\text{Ni py}_4\text{Br}_2$. The field due to the bromide ion therefore assumes two very different values in two closely related complexes: *ca.* 600 cm^{-1} in $\text{Ni py}_4\text{Br}_2$ but only *ca.* 350

cm^{-1} in $\text{Ni pz}_4\text{Br}_2$. As $Dq(\text{Br})$ *ca.* 600 cm^{-1} represents the spectrochemical series value,⁴ the unusually small $Dq(\text{Br})$ observed in $\text{Ni pz}_4\text{Br}_2$ must be interpreted in terms of specific properties of this complex.

Several structure determinations have established that ligands which contain both >N and >N-H groups may utilize them in co-ordinate (>N) and hydrogen (>N-H) bonds. In pyrazole these bonding groups are adjacent and the hydrogen bonds may be directed toward atoms either outside or inside the co-ordination sphere. External utilization occurs in the structure of $\text{Ni pz}_6(\text{NO}_3)_2$ which consists of Ni pz_6^{2+} cations linked to adjacent NO_3^- anions by six $\text{N-H} \dots \text{O}$ hydrogen bonds of 2.87 Å. The co-ordination about the nickel ion comprises six >N atoms in a nearly regular octahedral configuration. This co-ordination accounts for the regular octahedral band pattern observed in the visible spectrum of $\text{Ni pz}_6(\text{NO}_3)_2$. Internal utilization of <N-N-H is found in the structure of $\text{Ni pz}_4\text{Br}_2$ which consists of linear Br-Ni-Br groups with four planar pyrazole molecules aligned with the Br-Ni-Br direction. In this orientation the N-H group, the co-ordinating nitrogen atom and the Ni-Br group lie in one

plane to within 2° . This configuration (I) permits the N-H group to point approximately toward the bromide ion.



In the closely related complex, $\text{Ni py}_4 \text{Br}_2$,⁵ the pyridine rings are inclined *ca.* 45° away from the Br-Ni-Br direction, the Ni-Br distance is shorter (2.58 \AA) and the field of the bromide ion is normal. Thus, the available structural evidence indicates that the hydrogen bond interaction between the bromide ions and pyrazole molecules results in a reduction in the effective field of the bromide ion. An entirely analogous structural and spectroscopic behaviour is noted in the corresponding chloride complexes.

I thank Dr. A. D. Mighell and Dr. A. Santoro for valuable discussions.

(Received, November 7th, 1968; Com. 1517.)

¹ D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 1966, **6**, 1092.

² C. W. Reimann, A. Santoro, and A. D. Mighell, *Acta Cryst.*, submitted for publication.

³ A. D. Mighell, C. W. Reimann and A. Santoro, *Acta Cryst.*, in the press.

⁴ B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, 1966, p. 242.

⁵ A. S. Antsishkina and M. A. Porai-Koshits, *Kristallografiya*, 1958, **3**, 684.