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Correspondence

On the Structure of Tetrakis(pyridine)iron(II) Chloride

Sir:

A recent article[1] reports a theoretical and experimental Mössbauer study of iron(II)–pyridine complexes. The conclusion reached from this work was that $Fe(py)_4Cl_2$ had a cis octahedral structure whereas $Fe(py)_4(NCS)_2$ and $Fe(py)_4I_2$ had trans octahedral structures. The conclusion regarding the structure of $Fe(py)_4Cl_2$ cast doubts upon the validity of several spectroscopic studies of iron(II)–pyridine complexes[2,3] which have all assumed that $Fe(py)_4Cl_2$ had the same trans octahedral structure as an X-ray structural determination[4] had shown $Ni(py)_4Cl_2$ to possess. In view of this contradiction we decided to pursue a limited crystallographic investigation in order to ascertain if $Fe(py)_4Cl_2$ was isotypic with $Ni(py)_4Cl_2$.

Single crystals of $Fe(py)_4Cl_2$ were obtained by recrystallization from pyridine. Precession photographs showed the crystals to have tetragonal symmetry with systematic absences consistent with the space group $I4_1/acd$ (D_{4h}^{20}), which was the space group found for $Ni(py)_4Cl_2$ and $Co(py)_4Cl_2$.[4] Lattice constants for $Fe(py)_4Cl_2$ obtained from low-order powder lines are $a = 15.82$ and $c = 16.96$ Å, which may be compared with values of $a = 15.9$ and $c = 17.0$ Å for $Ni(py)_4Cl_2$ and $a = 16.0$ and $c = 17.1$ Å for $Co(py)_4Cl_2$. These results can be considered as strong evidence that the complexes $Fe(py)_4Cl_2$, $Co(py)_4Cl_2$, and $Ni(py)_4Cl_2$ are, in fact, isotypic and $Fe(py)_4Cl_2$ must be considered to have a trans octahedral structure.

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