06.2–30 ELECTRON DENSITY STUDY OF Co(C₅H₅NO)₆(ClO₄)₂
AT 78K BY X-RAY AND NEUTRON DIFFRACTION. BY J. S. Wood
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The title complex is a member of the series of iso-
structural hexapyridine N-oxide complexes \( \text{M(C₅H₅NO)}\)\(_6\)\(\text{X}_2\)
which at room temperature crystallise in space group \(\text{R}3\)
with \(\text{Z}=1\). In addition to showing large trigonal
electronic structural distortions, the complexes also exhibit interesting cooperative magnetic effects at low
temperature which are dependent on the nature of the
anion \(\text{X}\), as well as the metal. In order to examine how
these electronic properties are reflected in the change
density distribution around the metal and in the co-
ordinated ligand, we have carried out low temperature
X-ray and neutron diffraction measurements for the
cobalt perchlorate complex. The X-ray data (10,994
measurements to \(\sin \theta /\lambda = 1 \text{ Å}^{-1}\) at 78K, 4,536
independent) have been used to calculate \(\text{X}(\text{core})\) deformation
density maps, while parameters obtained from the
neutron refinement (1,359 independent reflections to
\(\sin \theta /\lambda = 0.67 \text{ Å}^{-1}\) measured at 90K) have been used to calculate \(\text{X}-\text{N}\) maps. The neutron analysis shows the
presence of a small amount of DIF solvent molecules
coordinated to the metal, such that the composition of
the crystal used for this analysis is actually
\(\text{Co(C₅H₅NO)}\)\(_6\)\(\text{ClO₄})\(_2\). Such sets of deformation
maps show aspherical features around the cobalt
atom attributable to the d-orbital density together
with bonding and lone-pair features associated with
the pyridine oxide ligand. The X-ray data are
currently being analysed using multiple refinement
methods and these results, together with a comparison
with those reported for the free ligand, will be given.