

s2.m1.p13 Fluorine the difficult atom in charge density analysis. H.O. Sørensen and S. Larsen, *Centre for Crystallographic Studies, University of Copenhagen*.
Keywords: charge spin densities.

The charge density modeling of the compound R-(+)-*p*-fluoromandelic acid (PFMA) lead to a highly contracted octopole on the F atom¹. This raised the question whether it was an artifact due to the lack of phase restrictions in the polar space group C2 or the poor description of the hydrogen atoms, as no neutron parameters were available. To resolve this question we have chosen the compound tetrafluoro-terephthalonitrile (TFT) as a model compound, studied earlier by Dunitz *et al.*² It contains no hydrogen atoms and crystallizes in the centrosymmetric space group Cmc₂ (1/4 molecule in the asym. unit).

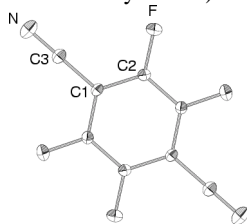


Figure 1: Ortep drawing of TFT. The envelopes are drawn at the 50 % probability level

32931 reflections to a resolution of 1.275\AA^{-1} were collected on TFT at 122.4(5)K using an Enraf-Nonius CAD4 diffractometer. These were reduced to 3239 independent reflections with a R_{int} of 1.3%. The multipole refinement resulted in a similar behaviour of octopole radial parameter on the fluorine atom as in PFMA. Since this could be caused by an insufficient description of the atomic displacement parameters, a high angle refinement (data with $\sin\theta/\lambda > 0.85\text{\AA}^{-1}$) of TFT including third order Gram-Charlier coefficients was performed. This model was used in the multipole modeling using all data. By this procedure the octopole radial parameter on the F atom converged at a physical reasonable value.

s2.m1.p14 Ferrimagnetic Ordering in a 'Ferromagnetic' Molecular Magnet. J.A. Stride,¹ B. Gillon,¹ A. Gukasov,¹ J. Larionova^{2,3} and O. Kahn^{2†}. (1). *Laboratoire Léon Brillouin, (CEA-CNRS), CEA Saclay, 91191 Gif-sur-Yvette Cedex, France*. (2). *Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS No. 9048, 33608 Pessac, France*. (3) *present address: UMR 5637, Université Montpellier 2, cc 007, Place E. Bataillon, 34095 Montpellier Cedex 5, France*. † *now deceased*.
Keywords: molecular magnetism, neutron diffraction, hydrogen bonding.

The synthesis of crystalline bimetallic, cyano-bridged, materials based upon Mo^{III} and Mn^{II} ions has been reported recently.¹ To date, three such systems have been isolated, dubbed α , β and γ phases. The γ phase is really a distinct material, with the formula $\text{K}_2\text{Mn}^{\text{II}}_3(\text{H}_2\text{O})_6[\text{Mo}^{\text{III}}(\text{CN})_7]_2 \cdot 6\text{H}_2\text{O}$. Ferromagnetic interactions between all of the metals were inferred from magnetic susceptibility data with a ground state of $S=17/2$ and $T_c=39\text{K}$.^{1,2} We have used neutron diffraction to re-examine this compound and find that the magnetic interactions are not quite so elementary.

We report here the nuclear structure determination by neutron diffraction at $T=50\text{K}$ and the study of the magnetic phase by polarised neutron diffraction at $T=4\text{K}$, under an applied field of 3T. The structure determination, is in very close accord with the reported room temperature X-ray structure.^{1c} One advantage of neutron diffraction over that of X-rays, is the ability to accurately determine H atom positions within samples containing heavy elements. Our structure displays an extensive hydrogen-bonded network of coordinated and non-coordinated water molecules. Another advantage of neutron diffraction is the strong interaction with magnetic moments within sample materials. A very accurate determination of the magnetic structure factor can be obtained by taking the ratios of the diffracted intensities of spin polarised neutrons, with the incident neutron spin aligned parallel and anti-parallel to an applied field. Our analysis of such data to obtain the local spin densities at the atomic sites, suggests that the $S=1/2$ spins of the Mo^{III} ions oppose those of the $S=5/2$ Mn^{II} ions, with significant spin density occupying the nitrogen sites of the bridging cyano ligands. Our analysis is consistent with a ferrimagnetic ground state of $S=13/2$.

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