X-ray and neutron-diffraction studies of the crystal structures of the dicesium lithium hexacyanometallates of manganese(III) and chromium(III)

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Abstract

Crystallographic examination of samples of Cs₂Li[M^{III}(CN)₆] (M^{III} = Mn, Cr), prepared by an improved route, establishes the unit cells as very closely approximating to face-centered cubic with lattice constants \( a = 10.64(1) \) (M^{III} = Mn) and 10.75(1) Å (M^{III} = Cr). Although a few weak non-face-centered cubic reflections and splittings were detected by powder neutron diffraction, refinement in \( Fm3m \) was as good as in primitive cubic or tetragonal space groups. Single-crystal neutron-diffraction refinements in \( Fm3m \) yield bond lengths Mn–C = 1.980(5) Å, Cr–C = 2.03(1) Å, and C–N = 1.188(5) and 1.20(1) Å, respectively. At 4.2 K, neutron powder data indicate the presence of further non-face-centered lines for both compounds, with contraction of unit-cell parameters to 10.55(1) and 10.67(1) Å, respectively.

Introduction

Among crystals of the elpasolite-type salts, Cs₂M^{I}M^{III}(CN)₆, those with \( M^{I} = \text{Li} \) have received appreciable study by diffraction and vibrational spectroscopy. The first-row transition-metal hexacyanides, Cs₂LiM^{III}(CN)₆ (M^{III} = Cr, Mn, Fe, or Co), form a closely related approximately isostructural low-spin series (Armstrong et al., 1973; Swanson and Ryan, 1973) in which similarity
of high-symmetry environments for the \( M^{III} \) ion should facilitate comparison of \( \sigma \) and \( \pi \) contributions to metal–ligand bonding.

Earlier diffraction studies on crystals and powders with neutrons (advantageous for the location of Li, C, and N atoms in complexes containing metals of high atomic number) and X-rays (Swanson and Ryan, 1973; Chadwick et al., 1985) have established the unit cells of the Fe and Co salts to be very close to that of elpasolite \( (Fm\overline{3}m) \) at room temperature; least-squares refinements yielded reliable values for the atomic parameters. The approximation of the room-temperature structure of the Mn salt to \( Fm\overline{3}m \) is rather less close and there are bigger deviations at liquid-helium temperature. For \( \text{Cs}_2\text{LiCr(CN)}_6 \), deviations appear to be rather greater at room temperature, such that other space groups have been proposed: \( P4_2\overline{1}2 \) (Ryan and Swanson, 1974), \( P4/mn \) (Chowdhury et al., 1977; Chowdhury, 1978), and \( P2_1/n \) (Ryan and Swanson, 1978). However, the cubic structure is accepted at higher temperature and Ryan and Swanson (1976) have described the phase transformations in terms of distortions along lattice modes; \( \text{Li}^+ \) and \( \text{Cr(CN)}_6^{3-} \) occupy octahedral sites with \( \text{Cs}^+ \) ions fitting loosely into tetrahedral holes defined by the \( \text{Cr-C-N-Li} \) superstructure.

In view of the interest of these compounds for spin, charge-density, and spectroscopic measurements, we report here the preparation by improved methods of \( \text{Cs}_2\text{Li}[M^{III}(CN)]_6 \) \( (M^{III} = \text{Mn, Cr}) \) and the study of their powders (at 4 and 300 K) and single crystals at 300 K by X-ray and neutron diffraction.

**Experimental**

*Preparation of dicesium lithium hexacyanometallates(III)*

\( \text{Cs}_2\text{LiMn(CN)}_6 \)

\( \text{K}_3\text{Mn(CN)}_6 \), prepared according to Palmer’s (1954) method, was converted to \( \text{Cs}_2\text{Mn(CN)}_6 \) in the way described for the cobalt compound (Chadwick et al., 1985) except that 20\% KCN solution was used. Since a method analogous to that used for the cobalt compound was unsuccessful [\( \text{LiMn(CN)}_6 \) was too unstable to be isolated as a solid], \( \text{Cs}_2\text{LiMn(CN)}_6 \) was eventually prepared by direct reaction between \( \text{Cs}_3\text{Mn(CN)}_6 \) and LiCl in molar ratio 1 : 3 in 20\% KCN solution. Large single crystals were grown by allowing this mixture to evaporate slowly in the dark at 0–5°C. Piezoelectric measurements (Prof. W. G. Perdok) on a single crystal were negative.

\( \text{Cs}_2\text{LiCr(CN)}_6 \)

\( \text{K}_3\text{Cr(CN)}_6 \) was prepared by slow addition of a saturated solution of chromium(III) acetate to a saturated solution of KCN. It was converted, in an anal-