

Electron Spin Resonance Evidence for Transfer of a Central Transition-metal Cation from One Set of Six Ligands to Another

By M. B. D. BLOOM, J. B. RAYNOR, and M. C. R. SYMONS*
(*Department of Chemistry, The University, Leicester LE1 7RH*)

Summary The complex ion $[\text{Mn}(\text{CN})_5\text{NO}]^{3-}$ can be incorporated into potassium chloride crystals without change; exposure to ^{60}Co γ -rays at room temperature gives a species whose e.s.r. spectrum is characteristic of Mn^{2+} in potassium sites in the crystal.

CONSIDERABLE evidence, both i.r. and e.s.r., shows that anionic complexes such as $[\text{Mn}(\text{CN})_5\text{NO}]^{3-}$ can be incorporated in alkali-metal halide crystals by replacing $[\text{M Hal}_6]^{5-}$ units.^{1,2} On exposure to high-energy radiation it is generally found that these centres trap electrons

efficiently. We had expected therefore to obtain the d^7 ion $[\text{Mn}(\text{CN})_5\text{NO}]^{4-}$ from the manganese complex in potassium chloride, but at room temperature we obtained e.s.r. spectra clearly caused by spin-free d^5 manganese complexes. One, having a small zero-field splitting, had $A(^{55}\text{Mn}) = 105.5$ G and the other, with no zero-field splitting, had $A(^{55}\text{Mn}) = 95.5$ G. Both were isotropic with $g = 2.0$. The unirradiated material exhibited no e.s.r. spectrum.

The spectrum with h.f.s. of 95.5 G is identical with that for Mn^{2+} incorporated in potassium chloride,³ and we are forced to conclude that manganese ions have been constrained to leave the complex cyanide site in favour of a vacant potassium site. Since for charge neutrality, there must be cation vacancies near the manganese complex ions, this transfer is not as drastic as it might seem. Thus, in contrast with normal environments there are preformed vacant sites, and the movement of a manganese ion from its original site to these vacancies would be understandable

provided some mechanism exists for overcoming the barrier constituting the ligand bonding in the initial cyanide complex. We tentatively suggest that, concurrent with electron loss to give the d^5 complex, one or more ligands are also lost and/or reversed to give weaker bonding. [Conversion of cyanide into isocyanide has previously been postulated for such systems.¹] The manganese ion then moves, possibly *via* the site of an ejected ligand, into initially an asymmetric lattice site thus yielding an e.s.r. signal with a zero field splitting. Further migration would thus give the symmetrical ion. One factor bearing on the ease with which this occurs could be coulombic. Loss of Mn^{2+} leaves a $(\text{CN})_5^{5-}$ grouping which is coulombically ideal for the crystal. The $[\text{MnCl}_6]^{4-}$ unit is only deficient by one charge, whereas the parent d^5 complex, $[\text{Mn}(\text{CN})_5\text{NO}]^{2-}$ is short of three negative charges, which is highly unfavourable.

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² H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, 1965, **42**, 3034; L. H. Jones, *ibid.*, 1962, **36**, 1400.

³ F. W. Breivogel and V. Sarkissian, *J. Chem. Phys.*, 1968, **48**, 2442.