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X-Ray Molecular Structures of Pentagonal Bipyramidal M(DAPSC)(NCS)$_2$, M = Mn or Ni, and EPR Spectra of Seven-Coordinate Mn(II) in these Compounds

M. V. CAPPARELLI, P. DE MEESTER, D. M. L. GOODGAME, S. J. GUNN and A. C. SKAPSKI

Chemical Crystallography and Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY, U.K.

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The EPR spectra of high-spin Mn^{II}, and the zero-field splitting (zfs) parameters derived from them, have proved to be useful probes in the study of the stereochemistry, both of pure manganese(II) compounds, and also of those of other divalent metals, by doping with Mn^{II} [1]. Although a wide range of the principal coordination geometries, and distortions from these, has been studied in this way [2], information is lacking about the EPR spectra of seven-coordinate Mn^{II}.

A particularly extensive series of seven-coordinate complexes is formed by 2,6-diacetylpyridine-bis(semicarbazone) (DAPSC), the structures of which have been studied by Palenik and co-workers [3]. During the course of a study of the EPR spectra of seven-coordinate manganese(II) using these compounds as host lattices we have prepared Mn(DAPSC)(NCS)$_2$ and Ni(DAPSC)(NCS)$_2$·2H$_2$O, using the general method of Wester and Palenik [4].

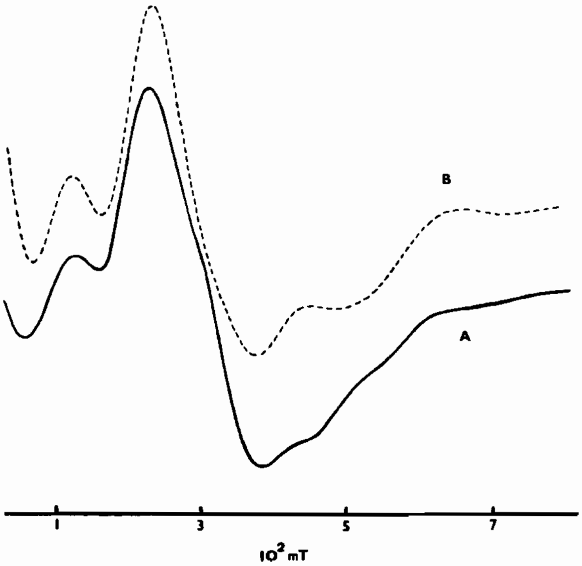

Fig. 1. A: X-Band spectrum of Mn(DAPSC)(NCS)$_2$; B: Simulated spectrum with D = 0.1 cm^{-1}, λ = 0.25.

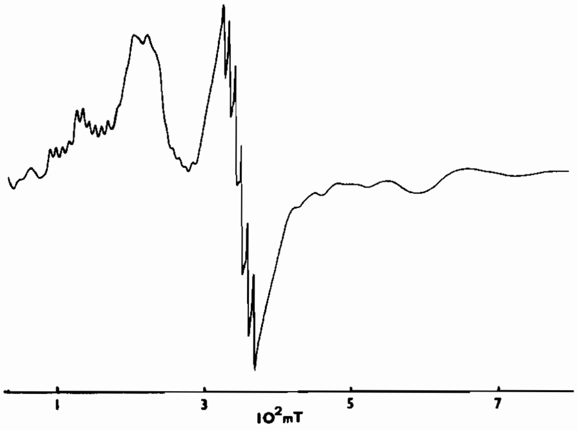

Fig. 2. X-Band spectrum of [(Ni,Mn)(DAPSC)(NCS)$_2$]·2H$_2$O.

The X-band EPR spectrum of a powdered sample of Mn(DAPSC)(NCS)$_2$ is shown in Fig. 1. Simulation of this spectrum, using the programme SHAPE9 [5] gave reasonable agreement for the zfs parameters D = 0.1 cm^{-1} and λ = 0.25 (λ = E/D).

The resonance fields of the main bands in the analogous spectrum of the nickel complex doped with manganese(II) (1 mol % nominal) differed from those of the pure manganese compound (Fig. 2). In this case, the presence of the manganese nuclear hyperfine components on some of the bands facilitated the spectral analysis (using the programme ESRS [6]). The zfs parameters obtained, D = 0.06 cm^{-1} and λ = 0.2, differed sufficiently from those of the pure manganese compound to suggest that there were differences in the environments of the manganese(II) ions in the two lattices. We have, therefore, determined their structures by X-ray methods.

Crystal Data and Structural Results

Complex **I**, [Mn(DAPSC)(NCS)$_2$]: C$_{13}$H$_{15}$N$_9$MnO$_2$S$_2$, triclinic, a = 8.825(1), b = 13.891(2), c = 16.986(3) Å, α = 109.68(1)°, β = 90.13(1)°, γ = 104.64(1)°, U = 1889.0 Å^3, space group $P\bar{1}$, Z = 4, D_c = 1.58 g cm^{-3}.

Complex **II**, [Ni(DAPSC)(NCS)$_2$]·2H$_2$O: C$_{13}$H$_{19}$N$_9$NiO$_4$S$_2$, triclinic, a = 8.747(1), b = 11.245(1), c = 12.543(1) Å, α = 114.23(1)°, β = 95.16(1)°, γ = 108.19(1)°, U = 1067.7 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.52 g cm^{-3}.

For both compounds X-ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using graphite-monochromated Cu-Kα radiation and an ω-scan technique. The total number of independent reflections measured was 4050 (to

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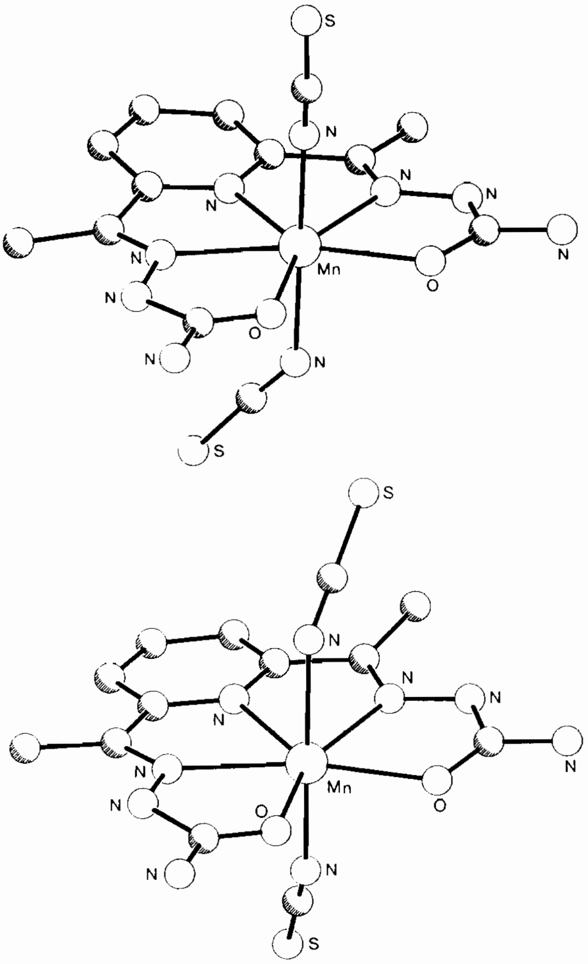

Fig. 3. View of the structures of the two crystallographically independent molecules of Mn(DAPSC)(NCS)$_2$, showing the different orientations of the NCS moieties relative to the equatorial plane.

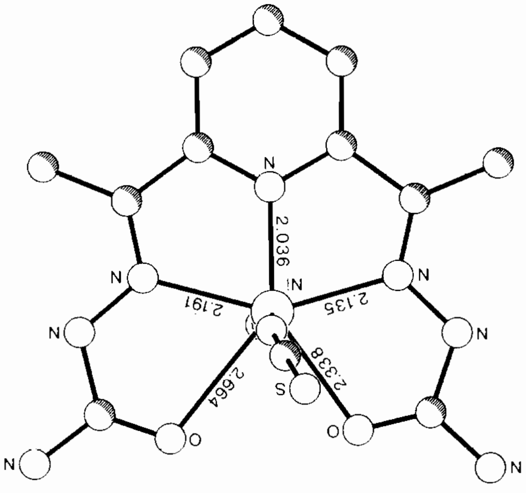

Fig. 4. View of the molecular structure of Ni(DAPSC)-(NCS)$_2$, showing the asymmetric bonding in the equatorial plane. The two axial bond lengths Ni–N(thiocyanate) are 2.004(4) and 2.011(3) Å.

θ = 50°) for I and 2860 (to θ = 55°) for II, of which 320 (I) and 131 (II) were considered 'unobserved'. Both structures were solved by Patterson and Fourier methods and refined by least-squares techniques to R values of 0.043 (I) and 0.042 (II). The program system SHELXTL [7] was used throughout the calculations.

In both complexes (Figs. 3 and 4) the metal atoms have essentially pentagonal bipyramidal environments, with the pentadentate Schiff base in the equatorial plane and two N-bonded thiocyanato groups in the axial positions. The water molecules in **II** are present as molecules of solvation and are not bonded to the metal ion.

In **I** there are two independent complex molecules in the asymmetric unit. The only major difference between them lies in the conformations of the axially coordinated NCS groups. The average values for the bond lengths within the coordination sphere are: Mn–N(py) 2.328 Å, Mn–N(imino) 2.313 Å, Mn–O 2.240 Å, and Mn–N(thiocyanate) 2.209 Å. (e.s.d.s 0.003–0.005 Å).

The nickel complex, on the other hand, has a much more asymmetric coordination geometry (Fig. 4). All the Ni–N bonds are between 0.1 and 0.3 Å shorter than the corresponding Mn–N bonds, the largest difference being in metal–N(py). Since DAPSC has been shown to be a relatively rigid ligand, the displacement of the Ni towards the pyridine ring should be accompanied by a lengthening in the Ni–O distances. Indeed, one of the Ni–O bonds is 2.388(2) Å (*i.e.* 0.15 Å longer than the average Mn–O), while the other, 2.664(2) Å, is abnormally long. A less pronounced, but also asymmetric, lengthening of the equatorial Ni–O bonds in seven-coordinate nickel(II) complexes has been observed by Palenik *et al.* [4, 8], who attribute it to a Jahn-Teller distortion.

The SCN groups are essentially linear (S–C–N angle range 177.1(4)° to 179.6(3)°) and have very similar bond lengths. On the other hand, the considerable variation in their inclinations with respect to the equatorial plane (metal–N–C angle range: 128.3(4)° to 174.0(2)°), and their conformation with respect to the DAPSC ligand, suggest that their positions are mainly determined by packing forces. A virtually linear M–NCS system (Fe–N–C, 178.7°) has been reported [9] in a related complex formed by iron(II) thiocyanate with 2,6-diacetylpyridine-bis(thiosemicarbazone).

The differences observed for the EPR spectrum of **I** and of the Mn(II) ions doped into **II** are understandable in the light of the results of the X-ray study. The Mn(II) ions in **II** are unlikely to adopt exactly the same sites as the nickel ions because of the difference in ion size and the geometric requirements of the DAPSC ligand. Their environments will, however, differ from those in **I**, principally in the orientations of the NCS groups, which should be essentially similar for all the complex molecules (Ni and Mn) in **II**.

Acknowledgements

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