Spin Transfer through Hydrogen Bonding in $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$? *

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Z. Naturforsch. **48a,** 123–126 (1993); received October 14, 1991

A polarised-neutron diffraction experiment on $[Co(NH_3)_5(H_2O)][Cr(CN)_6]$ shows the unexpected features of spin populations on the cobalt ((0.5(2) e) and the "ammine" hydrogen (0.8(1) e in total) atoms. A local density approximation DV-Xα calculation on a unit that models the molecular geometry in the crystal returns features that are broadly in agreement with the experiment. The calculation also reproduces the major features of a charge density experiment on the complex, including the low (±1.6 e) charges on the ions, in place of the formal ±3 e.

Key words: Spin density; Hydrogen bond; Local density approximation calculation; Charge density; Spin transfer.

Introduction

An earlier polarised-neutron diffraction (PND) experiment on $Cs_2K[Cr(CN)_6]$ had shown strong features of covalence and spin polarisation in the $Cr(CN)_6^{3-}$ ion, as illustrated in the map of spin density in a plane perpendicular to an octahedral C_4 axis (Figure 1). A local density approximation DV-Xα calculation on the ion reproduces the major features of the map, as shown in Figure 2.

A PND experiment was carried out on $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ with the aim of confirming the magnitudes of the covalence and spin polarisation effects in the anion. This salt crystallises in the same rhombohedral space group, $R\bar{3}c$, as does $[Co(NH_3)_6][Cr(CN)_6]$, with the H_2O group disordered over the six octahedral positions around the cobalt atom in a well-understood fashion. The disorder poses no real difficulty in the interpretation of the PND or the associated charge density experiments. Each cyanide N atom has one hydrogen bond to an ammonia molecule on a neighbouring cation, giving a three-dimensional network.

Two crystals were studied at a temperature of 1.5 K and a magnetic field of 4.6 T. For one crystal, mounted with ***H*** along the unique ***c***-axis, 287 flipping ratios were measured. For the other crystal, mounted with ***H*** along ***a***, 214 flipping ratios were determined.

Results

The spin distribution obtained from the experiment had surprising features, in particular the presence of significant amounts of spin density on the cobalt atom and on the protons of the ammonia molecules, and possibly on their nitrogen atoms. In this case, because of the rhombohedral symmetry of the space group, it is more sensible to view the octahedral $[Co(NH_3)_6]$ and $[Cr(CN)_6]$ units in planes containing a three-fold axis. Maps of the spin density are shown in Figure 3.

An all-electron DV-Xα calculation was carried out on the model "dimer" of a $[Co(NH_3)_6]$ and $[Cr(CN)_6]$ unit in which the hydrogen bonding is "intra-molecular" rather than distributed as in the crystal, and there are only three such bonds per cobalt or chromium atom, rather than six. The bond lengths and angles simulate the crystal environment closely. The "dimer" is illustrated in Figure 4. The calculation, in the Unrestricted Hartree-Fock-Slater formalism, employed a single "double-zeta" or better numerical basis set for each function, upto to 4s on Co and Cr, to 2p on C, N

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* Presented at the Sagamore X Conference on Charge, Spin, and Momentum Densities, Konstanz, Fed. Rep. of Germany, September 1–7, 1991.

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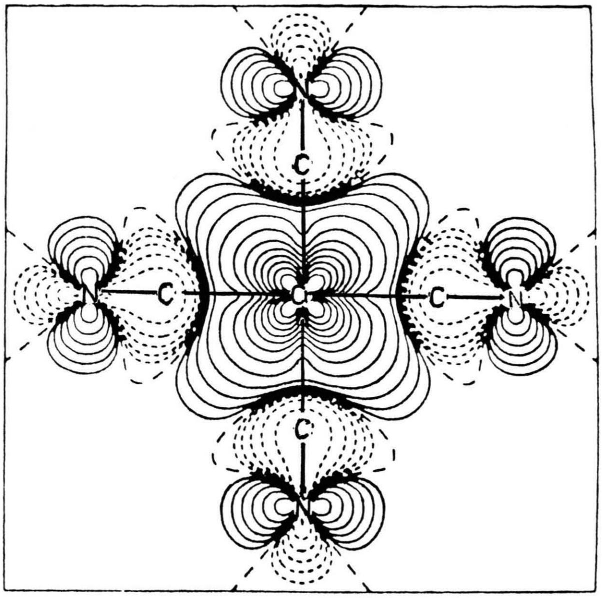

Fig. 1. At-rest spin density in a $Cr(CN)_4$ plane in $Cs_2K[Cr(CN)_6]$ from a multipole model.

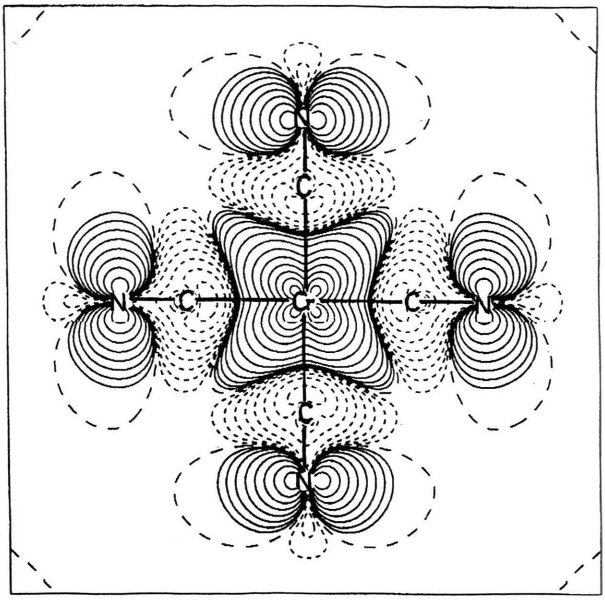

Fig. 2. Spin density in a $Cr(CN)_4$ plane of a $Cr(CN)_6^{3-}$ ion from a DV-Xα calculation.

Table 1. Experimental and calculated charge and spin valence orbital populations for salts containing the $[Cr(CN)_6]$ unit.

Populations	Charge					Spin			
	Experiment		DV-Xα calculation			Experiment		DV-Xα calculation	
	$[Co(NH_3)_6]$ $[Cr(CN)_6]$	Cs_2K $[Cr(CN)_6]$	$[Co(NH_3)_6]$ $[Cr(CN)_6]$	$Co(NH_3)_6^{3+}$	$Cr(CN)_6^{3-}$	$[Co(NH_3)_6(H_2O)]$ $[Cr(CN)_6]$	Cs_2K $[Cr(CN)_6]$	$[Co(NH_3)_6]$ $[Cr(CN)_6]$	$Cr(CN)_6^{3-}$
Co-3d	6.5(3)	–	7.28	7.23	–	0.3(1)	–	0.22	–
−4s/p	0.8(6)	–	0.84	0.93	–	0.25(6)	–	0.00	–
N′2s/p in H-bond	6.0(2)	–	5.75	5.77	–	0.01(1)	–	0.01	–
N′2s/p not in H-bond			5.72					0.01	
H 1s-2p in H-bond	0.7(1)	–	0.65	0.42	–	0.05(1)	–	0.22	–
H 1s not in H-bond			0.72	0.72	–	0.04(1)	–	0.01	–
H sp sum	–	–	–	–	–	0.82(6)	–	0.75	–
Cr-3d	3.1(3)	3.3(3)	4.13	–	4.19	2.28(1)	2.42(1)	2.15	2.93
−4s/p	0.8(6)	0.4(4)	0.88	–	1.10	−0.3(1)	0.0(4)	0.12	0.17
C-2s/p	4.3(2)	4.6(2)	4.18	–	3.78	−0.09(1)	−0.09	−0.10	−0.10
N-2s/p in H-bond	5.2(2)	5.5(2)	5.31	–	5.85	0.04(1)	0.05(1)	0.07	0.10
N-2s/p not in H-bond			5.23	–				0.04	
Cation/ anion charge	+1.4(4)	+1.6(4)	+1.76	+3.00	−3.00	–	–	–	–

The errors given in parentheses are from the least-squares refinement, or where available, from the agreement between repeat determinations.

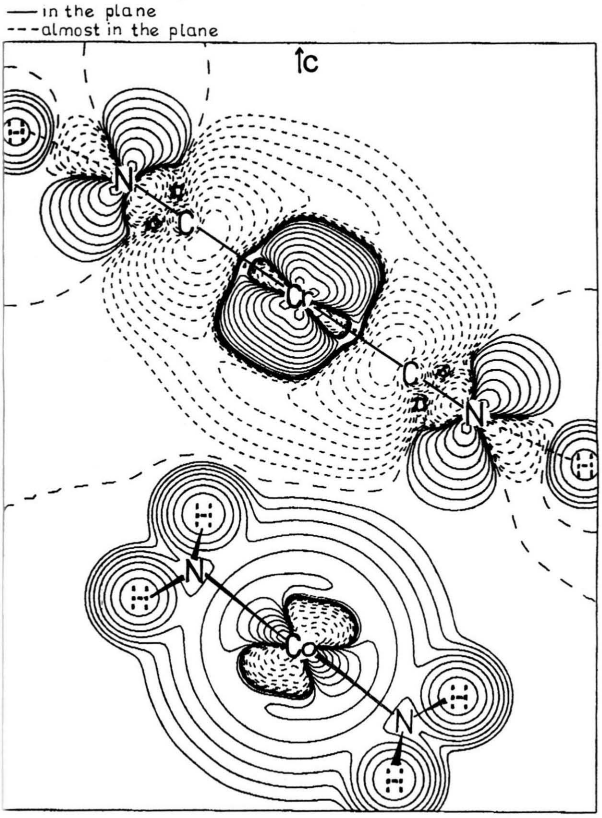

Fig. 3a. At-rest spin density in a plane in $[Co(NH_3)_6][Cr(CN)_6]$ containing Cr^{3+}, two CN^- and Co^{3+}; the NH_3 atoms are out the plane. The contours as for Figure 5. The map comes from a multipole model fitted to the PND data.

and the H atom in the hydrogen bond, and 1 s on the other H atoms. The functions were generated for atoms with the charges deduced by a previous calculation. The calculation used the "self-consistent charge" method of obtaining the intramolecular potential. The spin distribution produced by the calculation is shown in Figure 5.

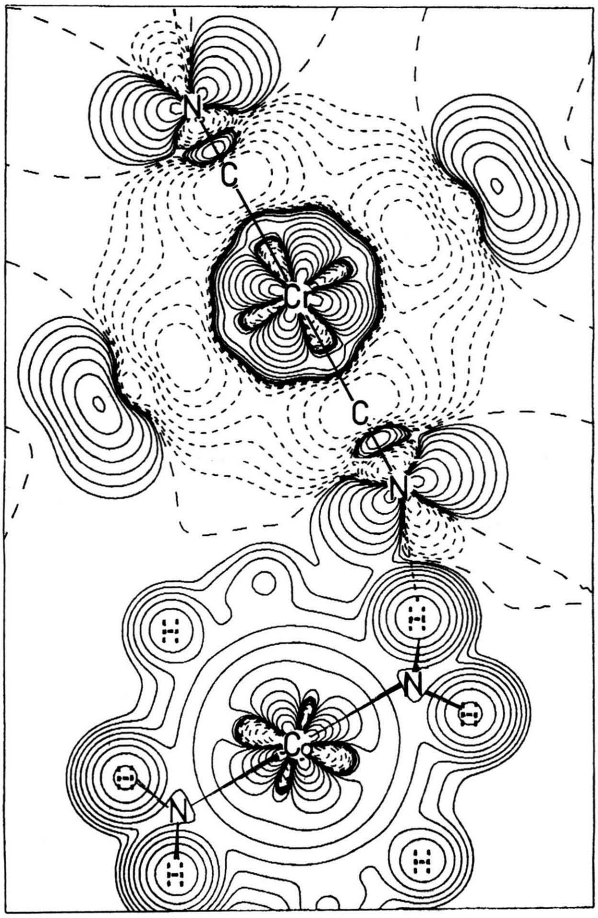

Fig. 3b. At-rest spin density in a plane in $[Co(NH_3)_6][Cr(CN)_6]$ containing Cr^{3+}, Co^{3+} and two NH_3 N atoms; the CN^- are out the plane. The contours as for Figure 5. The map comes from a multipole model fitted to the PND data.

In an attempt to make the comparison of the experiment and the calculation more quantitative than is possible using maps, population analyses in terms of the occupation of s, p, and d atomic orbitals was carried out. The least-squares refinement of the valence orbital populations from the experimental data yielded a goodness-of-fit (χ^2) of 0.97. This was compared with a Mulliken population analysis of the calculation. At this stage it is not possible to give details at the level of individual s-p hybrid or d orbitals. The two sets of quantities are rather different in nature, so their comparison is of limited validity. The exercise also provided the opportunity to include the results of a previous valence-orbital population analysis of the charge density experiments on $[Co(NH_3)_6][Cr(CN)_6]$ and $[Co(NH_3)_5(H_2O)][Cr(CN)_6]$. The results are given in Table 1.

Discussion

Comparison of the maps of Figs. 3 and 5 shows that the DV-Xα calculation reproduces the unexpected features of spin populations on the cobalt and the ammonia hydrogen and nitrogen atoms. Indeed, many of the populations in Table 1 show a surprising level of agreement, considering the limited accuracy of the experimental results, especially from the charge

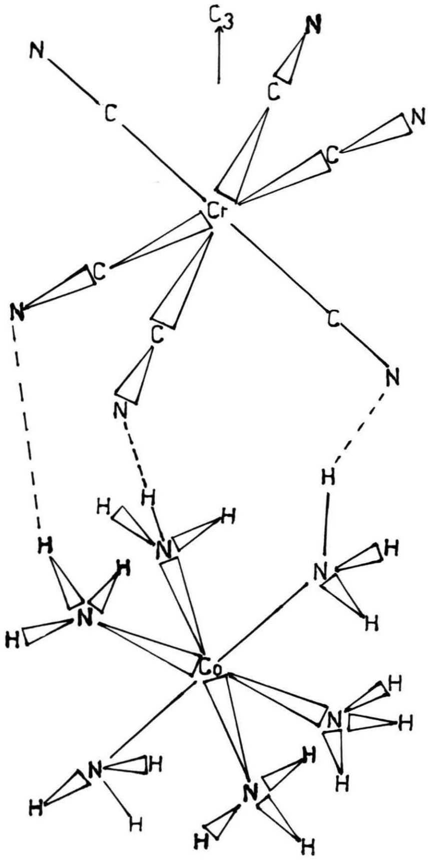

Fig. 4. The $[Co(NH_3)_6][Cr(CN)_6]$ "dimer".

density, and the crudeness of the model and the magnitude and limitations of the DV-Xα calculation. The spin seems to be carried from the anion to the cation region through the hydrogen bonds. However, there are obvious points of disagreement in the detail of the amounts and shapes of the spin distributions at the atomic centres. In particular, the experiment shows much more polarisation and diffuseness in the spin at the cobalt atom and more uniform hydrogen atom populations than does the calculation. The disagreements may arise to some extent because the maps, as produced from the multipole fitting procedure, contain details beyond the experimental resolution, but the different site symmetries of the crystal and the model "dimer" may be important.

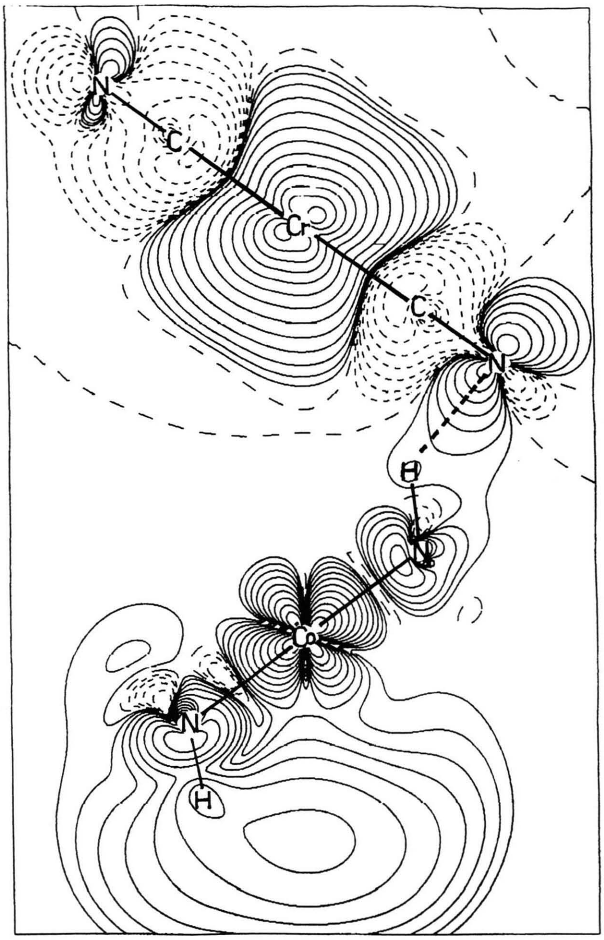

Fig. 5. The spin density in the $[Co(NH_3)_6][Cr(CN)_6]$ "dimer" in the plane of Fig. 4, from the DV-Xα calculation. The contours increase by a factor of 2.0, with the first at 0.0001 e a_0^{-3}.

NMR and ESR experiments to look for confirmation of the presence of spin on the cation have so far proved inconclusive.

We have previously suggested that the observation of appreciable spin on hydrogen-bonding ammonia protons provides an explanation for the antiferromagnetic exchange interaction in the complex $Ni(NH_3)_4(NO_2)_2$. However, in that case the effect is rather minor.

A more detailed presentation and discussion of these results will be published elsewhere [6].

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