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

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Abstract: The results of a polarized neutron diffraction (pnd) experiment on $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ carried out for two crystal orientations at 1.5 K with a magnetic field of 4.6 T are reported. Local density functional (ldf) calculations on models containing (a) the $[Co(NH_3)_6]^{3+}$ cation and one $[Cr(CN)_6]^{3-}$ anion and (b) one such cation and two such anions are presented. These models contain the major features of the hydrogen-bonding interactions in the crystal. Surprisingly, the pnd experiment shows the presence of substantial amounts of spin in the cation, located on both the cobalt atom and the ammine protons. The net spin population of the cation is about one-third of the total of the 3.0 unpaired electrons which arise from the $S = {}^3/_2$ d^3 system of the Cr^{3+} ion. As well as the net spin transfer to the cation, there is strong spin polarization, so that regions of negative spin, where the direction is opposite to that of the majority spin, are seen, including some on the cobalt atom. The spin density distribution in the $[Cr(CN)_6]^{3-}$ ion is distinctly different from that in the salt $Cs_2KCr(CN)_6$. The ldf calculations are in broad agreement with the pnd results in giving considerable spin transfer to the cation, with possibly a strong involvement of protons in the hydrogen bonds, and large spin polarization effects. However, there are many points of disagreement in detail, at least partly due to the fact that a simple model to reproduce the complex hydrogen-bonding arrangement of the crystal is not possible.

Introduction

Mainly on the basis of magnetic susceptibility measurements, weak magnetic-exchange coupling in transition metal complexes over separations involving many atoms has been postulated to be propagated through a pathway including a hydrogen-bond link.[1-9] In the case of $Ni(NH_3)_4(NO_2)_2$,[8] we obtained some confirmatory evidence from a polarized neutron diffraction (pnd) experiment which supported the presence of a small unpaired electron population on the bridging protons in the stronger hydrogen bonds. In charge density studies involving aquated metal ion salts, the cation and anion charges deduced are consistently considerably lower than the formal values,[10-13] and it can be supposed that the hydrogen bonds which link the units play a role in the transfer of charge. Also, small spin populations have consistently been observed on the water protons.[14] We reported charge density studies on $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$,[15,16] and these, along with a study on the $[Co(NH_3)_6]^{3+}$ salt,[17] led us to deduce that the cation and anion charges are much lower than the formal values of ±3.0. On comparing the results with another such study on $Cs_2K[Cr(CN)_6]$,[18] we were led to conclude that the N–H···N–C hydrogen bonding plays an important part in determining details of the electron distribution within the CN group of the anion.

The pnd experiment described in this paper was conducted principally to find whether certain important features of the spin density distribution seen in a pnd experiment[19] on $Cs_2K[Cr(CN)_6]$ were reproduced. In the event, equally interesting results concerning the transfer of spin from the anion to the cation were obtained, and we concentrate here also on that aspect. Because the results at first surprised us, we carried out some extensive theoretical calculations on systems containing the $[Co(NH_3)_6]$ and the $[Cr(CN)_6]$ units, both separate and bound together by hydrogen bonds. These calculations are most helpful in understanding the experimental results.

The principles of the pnd experiment and simple aspects of its interpretation have been set out by Tofield,[20] and his review covers early work. Brief surveys of some further results of chemical interest are available.[22] As applied to the present case, the electronic spin system of a single crystal of a paramagnetic substance is oriented in the direction of a large magnetic field, applied at a very low temperature. Neutrons, with their spin oriented alternately along and against the magnetic field, are incident on the crystal and are diffracted by the ordered array of the nuclei and also by the ordered array of the electronic spin magnetic moments in the crystal. Structure factors, F_N for the nuclear and F_M for the magnetic scattering, can be defined. The quantity measured by the experiment is the flipping ratio for a Bragg reflection, $R = I_\uparrow/I_\downarrow$. Here, $I_\uparrow$ is the scattered intensity of neutrons with spin aligned along the magnetic field direction ("up") and $I_\downarrow$ that of neutrons aligned against the field ("down"). With some simplification

$$R = (F_N^2 + 2F_NF_M + F_M^2)/(F_N^2 - 2F_NF_M + F_M^2)$$

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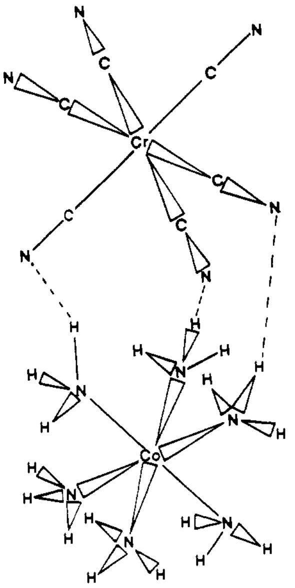

Figure 1. The "dimer" molecule of [$Co(NH_3)_6$][$Cr(CN)_6$] used for the ldf calculation.

From the measurement of R and the value of F_N from a separate low-temperature neutron structure experiment, F_M may be obtained.

For an orbitally nondegenerate system such as the ${}^4A_{2g}$ term of the Cr^{3+} ion of the present salt, it is possible to relate the magnetization density in the crystal defined by the values of F_M to the spin density distribution in molecular units. The relationship involves a scale factor which is close to half of the ESR g value. Studies such as those listed in refs 20 and 21 have shown that the spin density maps obtained for transition metal complexes are extremely informative on the chemical bonding present, particularly for the central metal atom and its first coordination sheath of donor atoms.

An understanding of the chemical bonding must, of course, be obtained by using theoretical calculations. The depth of information which is available from a pnd experiment is such that only ab-initio level calculations can do it justice. Empirical methods are not likely to be valuable. Furthermore, because unpaired spin is involved, electron–electron correlation effects must be included; results of the restricted Hartree–Fock type are not sufficient.[20,21] Since a configuration interaction approach to calculations for systems as large as transition metal complexes is out of reach, the unrestricted Hartree–Fock (UHF) procedure is the method of choice. While standard ab-initio UHF calculations on a simple transition metal complex are feasible, they are out of the question for complexes with many multiatom ligands.

Fortunately, recent developments have shown[22] that local density functional (ldf) methods can often produce results for chemical purposes of quality that is comparable or even superior to those of standard HF theory, as judged by reference to a full configurational interaction treatment, at a fraction of the computing effort. The ldf process replaces the nonlocal-exchange and correction terms in the Hamiltonian with estimates based on the density at the relevant point in space. In chemical usage, the ldf procedure may be referred to as the Hartree–Fock–Slater or Xα methods. Several ldf program suites are in use, and we adopt the discrete variational (DV–Xα) approach[23] which employs numerical atomic basis sets of high quality and numerical integration procedures. Using this method, we have been able to carry out calculations on units containing a great many atoms and still obtain results of useful accuracy.

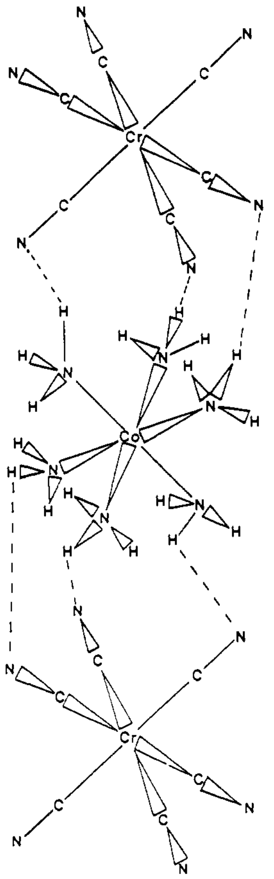

Figure 2. The "trimer" ion [$Co(NH_3)_6$][$Cr(CN)_6$]$_2^{3-}$ used for the ldf calculation.

Experimental Section

The same red-brown, somewhat ill-formed hexagonal columnar crystals of [$Co(NH_3)_5(OH_2)$][$Cr(CN)_6$] (space group $R\bar{3}$, a = 728.2 pm, α = 97.71°) that were used in the neutron diffraction structural studies[24,25] were employed. One crystal (6.4 × 2.5 × 2.5 mm) was mounted with the unique c axis nearly vertical in the D3 lifting arm diffractometer at the Institut Laue-Langevin. The flipping ratios of 287 reflections with $F_N(hkl) > 3.0$ fm were measured with a magnetic field of 4.60 (2) T at a temperature of 1.50 (2) K. Another crystal (5.5 × 2.6 × 2.6 mm) was mounted with the hexagonal b axis vertical, and 214 flipping ratios were measured. The data collection covered a period of 14 days. The neutron wavelength was 83.4 pm, and an Er filter suppressed $\lambda/2$ contamination. The polarization efficiency was 0.95 (1) and the flipping efficiency 1.000 (1). A standard reflection was measured after every 10 reflections and showed no deterioration in crystal quality over the duration of the experiment. Flipping ratios of >2.0 or <0.5 were excluded from the later refinements, as they may have been affected by multiple scattering effects.

Calculations at the unrestricted level using the DV–Xα program suite[23] were carried out on a PC equipped with an accelerator board.[26] Respective total numbers of integration points for [$Co(NH_3)_6$]$^{3+}$, [$Cr(CN)_6$]$^{3-}$, [$Co(NH_3)_6$][$Cr(CN)_6$] ("dimer", Figure 1), and [$Co(NH_3)_6$][$Cr(CN)_6$]$_2^{3-}$ ("trimer", Figure 2) were 9000, 9000, 30000, and 45000. The frozen-core approximation was employed. The basis sets, each equivalent to "double-ζ" quality, were as follows: Co and Cr, 3s–d,4s; C and N, 2s,p; H in H-bond, 1s,2s,p; H not in H-bond, 1s. Calculations employing more extensive basis sets and more integration points were also carried out on the [$Co(NH_3)_6$]$^{3+}$ and [$Cr(CN)_6$]$^{3-}$ ions to serve as benchmarks for the above more limited calculations which were necessary for comparison with the "dimer" and "trimer" units.[27]

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Table I. Results of the Refinement of the Valence Orbital Population Model for $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ Described in the Text

			b/c scale	0.987 (6)			
			Cation				
Co 3d $a_{1g}(\pi)$	−0.04 (7)	$e_g(\pi)$	−0.38 (13)	$e_g(\sigma)$	0.41 (15)	SP[b]	0.2 (1)
Co 4p (tot)	0.16 (7)						
H (av)	0.041 (5)						
			Anion				
Cr 3d $a_{1g}(\pi)$	1.05 (5)	$e_g(\pi)$	2.01 (9)	$e_g(\sigma)$	−0.7 (2)	r_{3d}	1.04 (1)
Cr 4p (tot)	−0.12 (8)						
C $p(\pi)$	−0.09 (2)	$(sp)_1$	−0.03 (2)	$(sp)_2$	0.06 (2)		
N $p(\pi)$	0.10 (2)	$(sp)_{1+2}$	−0.06 (2)				
		$R_w = 0.033$	$\chi^2 = 0.91$[c]	no. of variables = 21			

[a] Parameters not found to be significant in earlier modeling have not been included in this refinement. [b] SP is a mixing coefficient between the e_g orbital sets; see ref 15 for its definition. [c] "Goodness-of-fit".

Table II. Eigenvalues (eV) in the Region of the HOMO for the $[Co(NH_3)_6][Cr(CN)_6]$ "Dimer", the $[Co(NH_3)_6][Cr(CN)_6]_2$ "Trimer", and the $[Co(NH_3)_6]^{3+}$ and $[Cr(CN)_6]^{3-}$ Ions in the Same Geometry from the Calculations

$[Co(NH_3)_6][Cr(CN)_6]$[a]		$[Co(NH_3)_6][Cr(CN)_6]_2$[b]		$[Co(NH_3)_6]^{3+}$[c]		$[Cr(CN)_6]^{3-}$[c]	
$21E^+$	−5.1423	$16E_g^-$	1.0476	$9A_1$	−18.6647	$12E_g^+$	7.1332
$21E^-$	−5.1029	$16E_u^-$	1.0748	10E	−18.5275[d]	$11A_{1g}^+$	7.1361[d]
$20A_1^+$	−4.4917	$17E_g^+$	2.2557	11E	−15.5849	$12E_g^-$	9.2919
$22E^+$	−4.4410[d]	$17E_u^+$	2.2765	$10A_1$	−13.0673	$11A_{1g}^-$	9.2958
$21A_1^+$	−4.4386	$16A_{1g}^+$	2.3902			$13E_g^+$	11.2039
$23E^+$	−4.3391	$15A_{2u}^+$	2.3969[d]			$14E_g^+$	12.9586
$22E^-$	−4.1332	$18E_g^+$	2.5137			$12A_{1g}^+$	12.9705
$20A_1^-$	−3.4137	$17E_g^-$	2.5984				
$21A_1^-$	−2.8975						
$23E^-$	−2.8529						
$24E^+$	−2.0276						

[a] C_{3v} symmetry. [b] D_{3d} symmetry. [c] C_{3v} and D_{3d} symmetries, with experimental bond lengths and angles as in the $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ crystal. [d] HOMO.

Results

The pnd flipping ratios were processed in the usual fashion[28] using the neutron structure factors from the structural investigation[25] to give magnetic structure factors, $F_M(hkl)$. After averaging, there were 125 and 70 unique reflections for the *b* and *c* axes, respectively. They are listed in the supplementary material.

The magnetic structure factors were calculated using a valence orbital population model similar to that employed for $Cs_2KCr(CN)_6$[19] but extended to allow also populations on the atoms of the cation. As described in the report on the structure of the complex,[25] the water molecule of the $Co(NH_3)_5(OH_2)$ unit is disordered over the six octahedral coordination positions around the cobalt atom, and there is an accompanying disorder of the N atoms of the $Cr(CN)_6$ unit over two positions. We examined the effects of this disorder on the refinements by using a more detailed model than that reported here. The effects are sufficiently small that they are satisfactorily covered by the description inherent in Table I of a $Co(NH_3)_6$ unit and a $Cr(CN)_6$ unit with averaged bond lengths.

On the metal atoms were the 3d $a_{1g}(\pi)$, $e_g(\pi)$, and $e_g(\sigma)$ orbitals together with the mixing coefficients between them, as allowed by the S_6 ($R\bar{3}$) site symmetry, and 4p orbitals. The $a_{1g}(\pi)$ and the $e_g(\pi)$ orbitals together correspond to the t_{2g} set of O_h symmetry. The effective radius of the 3d orbitals was treated as a variable for Cr. On the N atoms of the ammonia molecules, a set of sp^3 orbitals was provided, with $(sp^3)_1$ pointing at Co. On the H atoms, there was a 1s orbital. On the C and N atoms of the $Cr(CN)_6$ unit, sp hybrids were used, with $(sp)_1$ pointing at Cr and C, respectively, together with a pair of p_π orbitals on each. An overlap density in the center of the Cr–C bond was included.

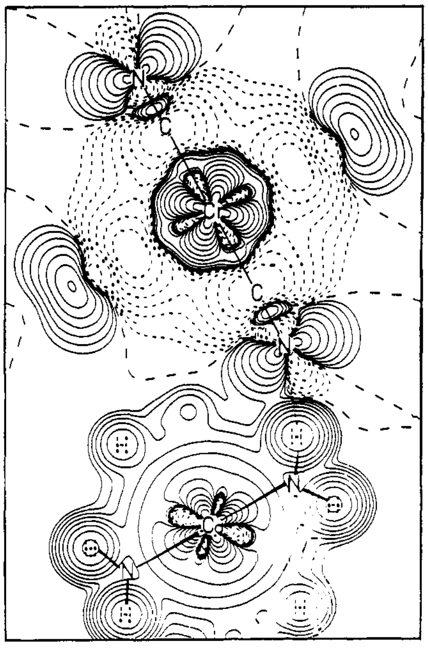

Figure 3. Spin density in $[Co(NH_3)_6][Cr(CN)_6]$ from a valence orbital population model of the pnd data. The plane contains major atoms of the cation and anion and almost one of the longer N–H–N hydrogen bonds. H atoms just out of the plane are entered in broken form.

The magnetic structure factors were refined in the above model using the least-squares program ASRED.[29] A study of the

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(27) These calculations employed 15 000 integration points, functions up to 4f on the metal atom and to 3d on C and N, and multipoles up to order 3 on the metal and 2 on C and N in the expansion of the potential in the self-consistent field refinement. Also, the atomic basis sets were obtained for atoms with fractional charges corresponding to the Mullikan population analysis of a previous calculation. The frozen-core approximation was retained. For comparison, the t_{2g}–e_g separations equivalent to the ligand field parameter Δ for, in order, the reference level, the "dimer"/"trimer" level, and the experimental spectral result are as follows: $Co(NH_3)_6^{3+}$, 2.88, 2.99, and 2.97 eV; $Cr(CN)_6^{3-}$, 3.82, 4.07, and 3.6 eV. Again, the reference level and "dimer"/"trimer" level 3d metal populations, respectively, are as follows: Co, total 7.359 and 7.226 e; Cr, total 4.189 and 4.242 e, spin 2.931 and 2.876 e.

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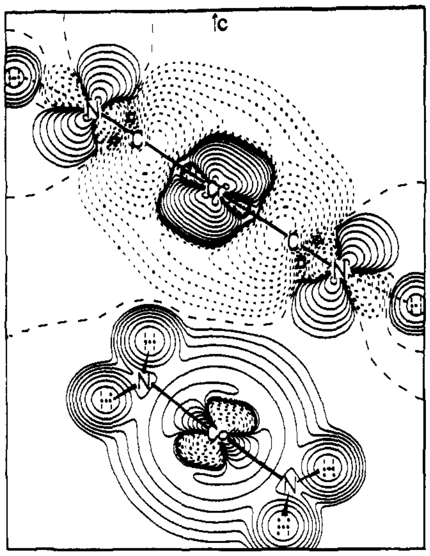

Figure 4. As for Figure 3, but the shortest N-H-N hydrogen bond is almost in the plane.

magnetic susceptibility and magnetization at very low temperatures has been carried out.[30] There is little if any magnetic exchange present (/*J*/ < 0.15 cm^{-1}), and a value of *F*(000) can be obtained. It was set at that deduced for the *c* axis direction, 8.94 (6) μ_B. The scale factor between the *c* and *b* axis F_M data was refined as the pnd experiment provides a more accurate relative measurement than does that of the magnetization. The value obtained, 0.987 (6), is in good agreement with that obtained from the magnetic susceptibility measurements, 0.99 (2).[30] The neutron structural study[25] showed that there was no need to consider the effects of extinction. The results of the refinement are given in Table I. The 3d mixing coefficients between the d orbitals on Cr were not found to be significant, but one of those on Co was above the level of significance. Maps of the spin density in appropriate planes containing the Co and Cr atoms are given in Figures 3 and 4.

The eigenvalues produced by the calculations in the region of the HOMO are listed in Table II. Maps of the calculated spin densities in appropriate planes containing the Co and Cr atoms are given in Figures 5 and 6. The more extensive calculations on the cation and anion showed that the results from the limited ones presented here are sufficiently accurate to support the comparisons we make with the "dimer" and "trimer" units. The populations of the basis set functions are within 0.02 e of the more accurate results, except those for the diffuse metal orbitals (0.1 e).[27] A calculation was also performed on the "dimer" unit in which the N···H-N distance had been increased by 2.0 au. Since the distribution of electrons among relevant atomic orbitals was not much altered, the results are not detailed here.

Discussion

Spin Density. In the earlier pnd investigation of $Cs_2KCr(CN)_6$,[19] it was found that the effects of spin polarization on the unpaired electron density distribution were comparable with those of covalence. "Down" (β, negative) spin was seen on the C atoms of the CN units, and it was not until the π system of the N atoms was examined that the expected transfer of "up" (α, positive) spin by covalence from the Cr atom appeared. These features were shown to be in qualitative agreement with theoretical calculations performed on the $Cr(CN)_6^{3-}$ ion,[31] and we have described their basis as "differential covalence" between the "up" and "down" spin manifolds. The initial thrust of the present investigation was to examine another $Cr(CN)_6^{3-}$ salt for similar behavior. Further

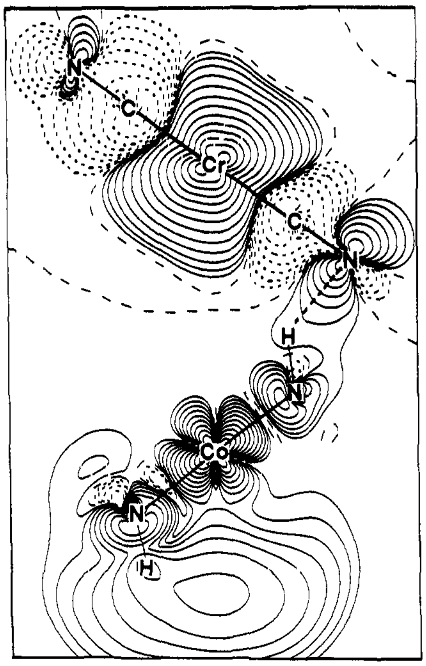

Figure 5. Spin density from the "dimer" molecule of Figure 1, in a plane which approximates to that of Figure 3.

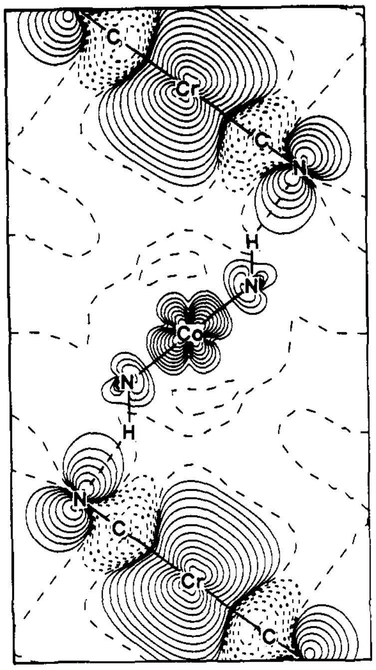

Figure 6. Spin density in the "trimer" ion of Figure 2, in a plane which approximates to that of Figure 3.

evidence for the importance of spin polarization in these covalently bound $M(CN)_6^{3-}$ complexes is now available from a pnd study of $Cs_2KFe(CN)_6$, but the picture there is confused by the orbital degeneracy of the $^2T_{2g}$ ground term in O_h symmetry, arising from the t_{2g}^5 configuration of the Fe(III) atom.[32,33]

These features of covalence and spin polarization and their explanation in terms of unrestricted Hartree–Fock theory are set out in Figure 7. There, the relative energies of some molecular orbitals from a DV-Xα calculation on the $Cr(CN)^{3-}$ ion are listed together with their approximate compositions in terms of the constituent atomic orbitals. Only those molecular orbitals with

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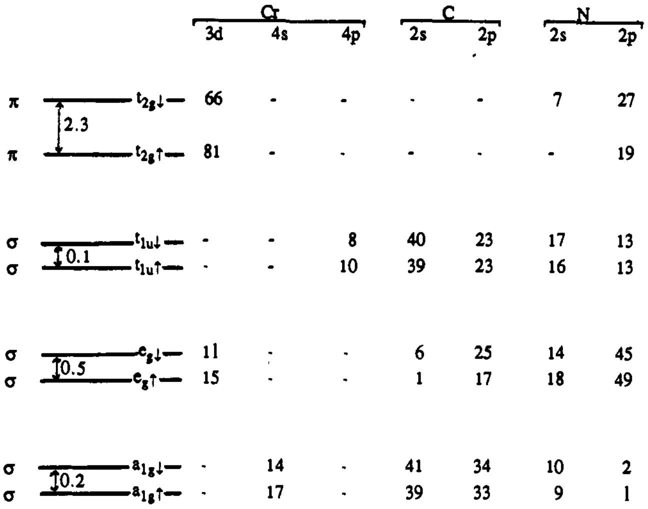
Table III. Calculated and Experimental Charge and Spin Populations (e) in the $Co(NH_3)_6$ and $Cr(CN)_6$ Species

		charge					spin				
		calculations			experiments		calculations			experiments	
		dimer	trimer	cation + anion	$[Co(NH_3)_6]$-$[Cr(CN)_6]$	$[Cs_2K]$-$[Cr(CN)_6]$	dimer	trimer	cation + anion	$[Co(NH_3)_6(OH)_2]$-$[Cr(CN)_6]$	$[Cs_2K]$-$[Cr(CN)_6]$
Co	3d t_{2g}	5.08	5.02	5.06	5.2 (2)		0.068	0.040	0.000	−0.4 (1)	
	3d e_g	2.24	2.24	1.09	1.7 (6)		−0.148	0.092	0.000	0.4 (2)	
	4s + 4p	0.84	0.92	0.93	0.9 (6)		0.000	0.005	0.000	0.16 (7)	
N	2s + 2p	5.74	5.73	5.78	6.0 (2)		0.009	0.006	0.000	0.00	
H[a]	1s–2p	0.65	0.48	0.63	0.7 (1)		0.223	0.000	0.000	0.04 (1)	
H[b]	1s	0.72	0.80	0.72	0.7 (1)		0.005	0.000	0.000	0.04 (1)	
Cr	3d t_{2g}	2.38	2.62	2.68	2.4 (2)	2.3 (4)	1.467	2.011	2.109	3.1 (3)	2.27 (3)
	3d e_g	1.74	1.62	1.56	0.8 (4)	0.6 (5)	0.684	0.747	0.767	−0.7 (2)	0.16 (3)
	4s + 4p	0.88	0.62	0.84	0.4 (3)	0.1 (4)	0.116	0.097	0.146	−0.12 (8)	0.88 (7)
C	2s + 2p	4.18	4.35	4.24	4.3 (2)	4.4 (2)	−0.100	−0.120	−0.119	−0.06 (2)	−0.09 (2)
N	2s + 2p	5.28	5.34	5.42	5.2 (2)	5.3 (2)	0.054	0.105	0.106	0.04 (3)	0.05 (2)
cation	charge	1.76	2.02	3.00	1.4 (4)	1.6 (4)					

[a] Hydrogen atom engaged in the hydrogen bonding. [b] Hydrogen atom not engaged in the hydrogen bonding.



		Cr 3d	Cr 4s	Cr 4p	C 2s	C 2p	N 2s	N 2p
π	t_{2g}↓	66	-	-	-	-	7	27
π	t_{2g}↑	81	-	-	-	-	-	19
σ	t_{1u}↓	-	-	8	40	23	17	13
σ	t_{1u}↑	-	-	10	39	23	16	13
σ	e_g↓	11	-	-	6	25	14	45
σ	e_g↑	15	-	-	1	17	18	49
σ	a_{1g}↓	-	14	-	41	34	10	2
σ	a_{1g}↑	-	17	-	39	33	9	1

Figure 7. 1% composition of Cr-containing molecular orbitals in a DV–Xα calculation on the $Cr(CN)_6^{2-}$ ion. Orbital energy separations are in units of eV.

a substantial Cr content are included.

The occupied "up" and "down" spin a_{1g} and t_{1u} σ orbitals, involving respectively the Cr 4s and 4p orbitals, differ little in energy, and the maximum composition difference is 3%. The covalence is reflected in the 8–17% Cr participation. The occupied e_g σ orbitals, involving the Cr 3d orbitals, have a somewhat larger "up"–"down" energy separation (0.5 eV) and distinctly larger composition differences (up to 8%), which are responsible for the spin polarization effects. These arise from the different amounts of covalent mixing in the "up" relative to the "down" spin orbitals. In particular, they are responsible for the remarkable net "down" spin on C and the absence of nodes along the Cr–C axes at the Cr atom in Figure 9. The nodes of the t_{2g} orbitals would have been obvious for a zero 3d e_g spin population. These effects are also seen clearly in the experimental spin density map (Figure 8).

The π t_{2g} orbitals show by far the largest differential covalence effects. The "up"–"down" spin splitting is 2.3 eV, and the "down" chromium and ligand coefficients are closer, corresponding to higher covalence. However, of course, only the "up" orbitals are occupied. It is through these orbitals that the majority of the covalent spin transfer takes place. It is to be noted that the covalently transferred spin is deposited on the N atoms of the cyanide ligands, in accord with observations (Figure 8).

This study does confirm the generality of the observations that there is substantial covalence in the Cr–CN bonding and that spin polarization can cause as much unpaired electron density shift as does the covalence. In the Cr atom in $[Co(NH_3)_5(OH_2)]$-$[Cr(CN)_6]$, there is a "down" spin population on the C atom of the $Cr(CN)_6$ unit, and the net spin population on the N atom is "up". The amounts of spin transferred by spin polarization and by covalence are comparable with those observed in $Cs_2KCr(CN)_6$ and support the results of the experiment on that compound. These points are set out in the last two columns of Table III. The picture in the UHF framework that the spin polarization through differential covalence arises because the better matching of the "down" relative to the "up" spin chromium d-manifold energies and radial extents with cyanide orbitals leads to greater "down" than "up" covalence is repeated.

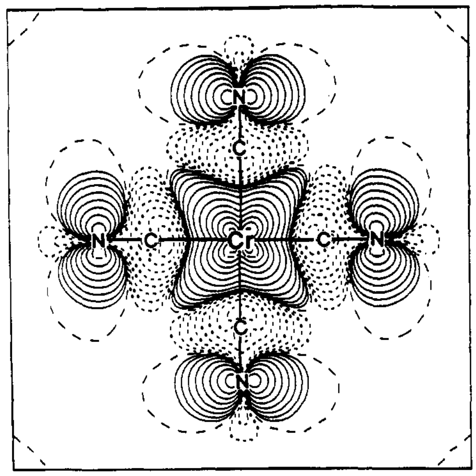


Figure 8. Spin density in a $Cr(CN)_4$ plane of the $Cr(CN)_6^{3-}$ ion in $Cs_2K[Cr(CN)_6]$, from a valence orbital population model of the pnd data.[18]

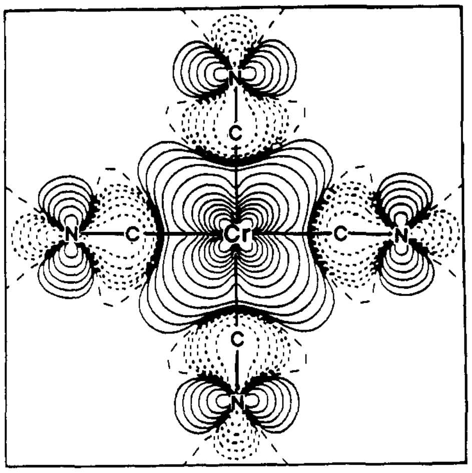


Figure 9. Spin density in a $Cr(CN)_4$ plane of the $Cr(CN)_6^{3-}$ ion, for a ldf calculation.[18]

In Figure 8, the spin density found in the $Cr(CN)_6$ unit in the Cs_2K salt is reproduced, and in Figure 9 that from an ab-initio ldf calculation is shown. There is obviously much similarity, and in the salt the unit closely resembles a $Cr(CN)_6^{3-}$ ion. However, there are important points of difference in the distribution of spin within the $Cr(CN)_6$ unit in $Cs_2KCr(CN)_6$ and in the present compound. The map of Figure 3 shows a section through the unit in $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ which contains the same $Cr(CN)_2$ moiety, the remaining two CN groups being tilted somewhat out of the plane. Here, there is much less similarity with either of the maps of Figures 8 and 9. In the present compound, the $Cr(CN)_6$ unit has features not expected for a $Cr(CN)_6^{3-}$ ion.

An examination of Table III helps to quantify the differences. The experimental "down" spin and the "up" spin populations on the C and N atoms are quite similar in the two complexes, but there appears to be much stronger spin polarization within the Cr atom of the $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ salt. The t_{2g} population is increased, at the expense of the e_g population, which becomes negative, that is, "down".

However, the more surprising feature revealed by Table III is the presence of spin populations on the $Co(NH_3)_6^{3+}$ cation. They are 0.16 (net) on the cobalt atom and smaller, but significant, values on the ammonia protons, which in total amount to even larger populations (0.7 e). The spin distribution on the cobalt atom is complex, with more or less equal regions of "up" and "down" spin, as seen also in Figure 2 and 3. Of the net 3.00 unpaired electrons of "up" spin per Cr atom, about 30% are located on the $Co(NH_3)_6$ group. Alternatively, of the total of 7.6 e[34] of "up" and "down" spin combined, about 20% is on that group. It seems that spin is transferred from the anion to the cation, evidently via the CN···H–N hydrogen-bonding pathway. In the earlier charge density studies[15,16] on the complex, it was suggested that charge transfer involving that pathway could be responsible for the low net *charges* deduced for the ions.

Calculations. In order to examine how likely it is that the hydrogen bonding provides a pathway for spin and charge transfer, the calculations mentioned above were carried out. These calculations were on models which reproduce the experimental bond lengths and angles, including those of the N···H–N bonding in the $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ crystal, quite closely. However, they do not reproduce the fact that in the crystal the hydrogen bonding is three-dimensional, with each cation so bonded to six different anions and vice versa. In the crystal, the site symmetry is S_6, whereas in the models, it is C_{3v} ("dimer") or D_{3d} ("trimer"). Consequently, the calculations do not reproduce the symmetry of the magnetic structure in the crystal. This means that their value in accounting for the magnetism-transfer process can only be illustrative.

The calculations on the models do support the presence of remarkably strong interactions between the anions and the cations, although there are some important disagreements between the two models and between them and experiment. The comparisons of the calculations and their relationship to the charge and spin density experiments are set out in Table III. Both of the calculations support the presence of spin density on the Co atom, with a total of ca. 0.22 e for the "dimer" and of 0.15 e for the "trimer" model, in each case involving only "up" spin and mostly concentrated in the 3d e_g orbitals, with almost negligible 4s/p participation. As noted above, the experiment gives a similar net amount of total spin, comparable amounts of "up" and "down" spin, and a strong 4s/p component. The "dimer" calculation gives a spin component on the bridging protons much higher than that from experiment, but the "trimer" calculation gives none. It is obvious that, as might be expected, the wave functions which carry spin across the hydrogen-bonding bridge are very sensitive to their symmetry. In the case of the "dimer" calculation, it is to be noted that a second MO of A_1^+ composition lies very close above one which carries one of the unpaired electrons, and this near degeneracy may be relevant to details of the unpaired electron distribution. An inspection of the compositions of these two MO's revealed no qualitive differences but significant quantitative differences in the amounts of Cr, Co, and bridging proton contributions. However, no pattern which would give a major change in the map of the spin density was obvious. The calculations on the models do not agree well between themselves or with the experiment about the Cr atom. They give results which fail to show the strong spin polarization with "down" spin in the 3d e_g orbitals, rather indicating "up" spin transferred from the t_{2g} set.

The model calculations and experiment agree reasonably well about the populations in the atomic orbitals of the ligands but not about the two metal centers and the bridging protons. There is essentially no spin on the ammonia N atoms, about 0.1 e "down" spin on the C atoms of the cyanide group, and about 0.05 e "up" spin on its N atoms. This gives some confidence that the prediction by the calculations of unusual behavior on the metal and the bridging proton atoms is to be taken seriously, even if not quantitatively.

Turning to the *charge* populations of the atomic orbitals, the calculations on the models agree between themselves and, within the obviously limited accuracy involved for such a large system, with experiment to an almost surprising degree. The expected considerable difference between the total ammonia N (5.7–6.0 e) and the cyanide N (5.2–5.4 e) valence orbital populations is reproduced. The only significant disagreement is in the Cr 3d e_g population, where the low experimental results presumably reflect the spin polarization not seen in the calculations. Spin polarization is known to be a result of configuration interaction. The UHF calculations employed here include an ill-specified amount of configuration interaction and cannot be expected to account for such an aspect of the experiment particularly well.

The magnetic susceptibility results[30] show that magnetic exchange in the compound is almost negligible ($|J| < 0.2$ cm^{-1}). In view of the magnetization transfer through the hydrogen bonding, this result is perhaps surprising. Magnetic-exchange integrals of appreciable size have been seen to arise from that mechanism over distances greater than the Cr···Cr separation in the present complex.[1-9] However, as mentioned above, magnetic ordering in a substance is critically dependent on symmetry considerations, and there is much symmetry in the crystal. Furthermore, the calculation on the "trimer", although showing spin on the central cobalt atom, gave the $S = 3$ ground state expected for two uncoupled $S = {}^3/_2$ $Cr(CN)_6^{3-}$ ions, with no splitting such as might be expected if magnetic exchange were present.

Other Experiments

A search for evidence for the presence of spin on the pentaammineaquacobalt cation using experiments other than pnd has not yielded definitive results. The ESR spectrum at 77 K[35] shows an anomalous, although small, *g* anisotropy and large and varying line width, relative to say $Cs_2KCr(CN)_6$, but no definite interpretation is available. ^1H solid-state NMR is not observed, presumably because of excessive line widths from the paramagnetism. In the case of ^{59}Co, there appears to be a relatively small, but possibly significant (600 ppm), upfield shift relative to the result in solution. However, we await the outcome of further ESR and NMR studies on crystals of $[Co(NH_3)_5OH_2)][Co(CN)_6]$ and other related systems before commenting further.

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Supplementary Material Available: A list of observed and calculated magnetic structure factors for the refinement (2 pages). Ordering information is given on any current masthead page.

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[34] This figure is deduced from details of the refinement, which are given in Table I, by summing irrespective of sign, the orbital populations listed, multiplied by the number of atoms (6 for C and N, 18 for H) with which they are associated.

[35] Figgis, B. N.; Kucharski, E. S.; Manoharan, P. T. Unpublished work. $g_a = g_c = 0.08$, versus $(\Delta g)_{max} = 0.01$ for $Cs_2KCr(CN)_6$.