Charge Density in $[Ru(ND_3)_6][SCN]_3$ by X-Ray Diffraction at 92 K *

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High quality X-ray data were collected on a $[Ru(ND_3)_6][SCN]_3$ crystal at 92 K. All 7531 unique data were analysed with multipole and with valence-orbital population models of the charge density to give $R(I)$ as low as 0.017 with χ^2 0.88. The model suggests substantial σ donation from the ammonia molecules [0.65(7) e] to the ruthenium atom, but almost negligible π donation [0.09(7) e], as expected. The 4d charge distribution on the ruthenium atom is essentially cubic in symmetry $[4d_{xy}^{1.61(5)}4d_{xz}^{1.63(5)}4d_{yz}^{1.67(5)}]$. A general ligand-field model, derived from the highly anisotropic magnetic data on crystals, predicts just such an almost cubic 4d-electron distribution. The hole in the Ru^{III} t_{2g}^5 configuration ($^2T_{2g}$ ground state) is not in this case localised into a non-cubic t_{2g} orbital population because the spin-orbit coupling dominates the rhombic components of the ligand field. Charge transfers are also found from the thiocyanate anion to the ammonia molecules. As contact distances from ND_3 to NCS decrease, substantial charge is transferred from SCN to ND_3. In addition the ND_3 molecule becomes more polarised, with charge migrating from D to N and the SCN group becomes polarised, with charge migrating towards the centre. These 'intermolecular' or crystal effects result, as judged by agreement factors, in very significant differences in the charge distributions on the three crystallographically distinct ammonia groups and the two distinct thiocyanate ions.

Careful experimental charge-density studies of small molecules performed at low temperatures are now accepted to lead to electron-density distributions which agree with sufficiently high-level theoretical chemical calculations. Together, these techniques provide valuable chemical insight into the formation and behaviour of such molecules. For the first transition-series complexes the position is, of course, much less favourable because of the much greater relative contribution to the scattering from the core electrons. However, recent studies have demonstrated that by employing low temperatures quite worthwhile information can be obtained from the complexes of the first series. This arises at least in part because the radial extent of the 3d orbitals is such that their scattering is in a range of Bragg angles somewhat different from that from the core electrons, and where the X-ray data is least affected by systematic errors from extinction and atomic displacements, and so is most accurate.

The position for the second transition-series complexes is obviously even less favourable than for the first series because of the larger cores. However, the point that the scattering from the d electrons can be isolated is still valid. This occurs because of the different dependence in Bragg angle from that of the cores and their displacements at very low temperatures. Although early charge-density results from heavy-metal complexes produced little clear chemical information, some recent studies which did employ low temperatures have been more encouraging.[1,2] Here we make a study of a classical second transition-series complex, $[Ru(ND_3)_6][SCN]_3$, at a moderately low temperature, concentrating in particular on details of the 4d-electron distribution and its relationship to ligand-field theory. However, we find that we are also able to extract important chemical information about aspects of the electron distribution arising from the s and p valence electrons.

The single-crystal magnetic properties of some complexes containing transition-metal ions in low-symmetry ligand environments and with substantial orbital contributions to the moments have been explained with a five-parameter ligand-field model involving only the t_{2g} orbital basis set. For the $^5T_{2g}$ state of Fe^{II} (d^6) in $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$,[3] the $^2T_{2g}$ state of Fe^{III} (d^5) in $Cs_2K[Fe(CN)_6]$[4] and the $^2T_{2g}$ state of Ru^{III} (d^5) in $[Ru(ND_3)_6][SCN]_3$[5] the ligand-field model is unusually convincing in that the observation-to-parameter ratio is high.

We can further test the t_{2g} basis model experimentally to examine its adequacy. Diffraction experiments are useful for such a test, in that they probe the spatial consequences of the ligand-field model, as opposed to the energetic consequences reflected by magnetic, ESR and spectroscopic studies. At a more abstract level, spectroscopy averages over the crystal, and resolves time but not distance. Elastic diffraction, as here, also averages over the crystal but, conversely, resolves distance but not time.

A polarised neutron diffraction (PND) study of $Cs_2K[Fe(CN)_6]$[6] showed that the cubic component of the ligand field, determined by the ligand octahedron, does indeed dominate the spatial distribution of the magnetisation, while the low-symmetry component, as reflected in the splitting and mixing of the t_{2g} orbitals in the model, does not. However, the latter component still explains the total magnetisation distribution and its direction, which is canted away from the magnetic-field direction.

An X-ray diffraction study of the d-electron distribution is a similar test, although experimentally more demanding. Both $(ND_4)_2Fe(SO_4)_2 \cdot 6D_2O$[7] and $Cs_2K[Fe(CN)_6]$[8] have been examined by that technique. In both cases it appears that the d-electron distribution is more cubic than the respective ligand-field models might predict. However, this conclusion is complicated in the former case because the experimental temperature is not small compared with the splitting between the ground and the excited states, and in the latter case by large covalence.

We present here a low-temperature X-ray diffraction study of $[Ru(ND_3)_6][SCN]_3$. In this complex we expect the π covalence to be very small, and the ligand-field model suggests that the experimental temperature is small compared with the splitting between the ground and excited states. Thus any deviation from the predictions of the t_{2g} model cannot be explained away as easily as in the former cases. In addition, in this case, the ligand-

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

field axis system does correspond roughly with the ligand octahedron axes. Thus we believe that in this case the t_{2g} based ligand-field model is likely to be close to the correct full d manifold fourteen-parameter model. The new feature here is the study of a 4d rather than 3d system. Contrary to some expectations, we find that the extra difficulty associated with the larger metal core does not, in practice, reduce the experimental accuracy markedly. We note that a recent study at 85[9] and at 9 K[10] has elucidated and clarified the systematic errors which are present in charge-density experiments, and shows that, provided appropriate models are used, and a somewhat lower accuracy overall is accepted, studies at liquid nitrogen temperatures in complexes of the transition metals give reliable results.

Experimental

The charge-density experiment is now sufficiently routine at liquid nitrogen temperatures that here we only summarise the conditions we employed (for a full description of the procedures see refs. 7–9).

The compound, prepared as before,[5] was recrystallised twice from D_2O and a suitable crystal was mounted. A complete sphere of data was collected, using conditions summarised in Table 1. The only improvement introduced over previous practice[7–9] was use of the profile-fitting program PROFIT[11] to analyse the reflection scan data. At low temperatures deuteriation provides a useful improvement by appreciably reducing thermal motion, particularly on hydrogen sites.

Models and Refinements.—Studies of the ammonium–copper Tutton salt, $(ND_4)_2Cu(SO_4)_2{\cdot}6D_2O$, at 9 and at 85 K[9,10] have clarified what features of refinement are relevant to model charge-density quality X-ray diffraction data collected at liquid nitrogen temperatures for first transition-series complexes. They include (*a*) the treatment of apparent anharmonicity in the atomic displacements. (*b*) Besides the usual radial flexibility provided for the functions describing the valence density, the non-metal, non-hydrogen atoms require special treatment. (*c*) The use of a full multipole scheme is not much improvement on a chemically based valence-orbital approach outlined in (*b*). (*d*) The use of neutron diffraction to fix core positional and atomic-displacement parameters (X–N procedure) is probably not appropriate.[12]

In the models of the present study we have used anharmonic-displacement parameters in a Gram–Charlier expansion to fourth order on ruthenium, and to third order on other non-hydrogen atoms, a Type II extinction correction, and an empirical two-parameter multiple-scattering correction. We have assumed that SCN densities retain cylindrical symmetry. Atom-form factors, anomalous-dispersion corrections, and refinement program were as previously described.[9,10] Starting parameters were taken from the 295 K study of the compound.[5]

In this work we examined both the conventional multipole and our own valence-orbital population analyses of the charge density. Valence-orbital population models are less rigorous than multipole models, though even with the latter truncation of multipole order and choice of radial functions are arbitrary features. They do however, offer the advantages of involving fewer parameters and being chemically more transparent.

The multipole model employed was to order four on the Ru 4d, thiocyanate S 3(s/p), C 2(s/p) and N 2(s/p) radial functions; order three for ammonia N 2(s/p); order two for Ru 5(s/p); and order zero for D 1s, and the extra S, C and N diffuse functions which were introduced,[10] as were the mid-bond overlap densities for the Ru–N, S–C and C–N bonds.

The valence-orbital population model incorporated nine 4d and three 5p ruthenium-based functions; sp^3 hybrid orbitals on the ammonia N atoms; sp^1 and p_π orbitals on the atoms of the thiocyanate ion; and spherical diffuse hydrogen 1s; and bond-overlap Gaussian functions. As in the multipole model, 'kappa' refinement[13] of all the main valence shells was performed, except at the disordered SCN site. The ruthenium quantisation axes were z//Ru–N(12), with x//Ru–N(11). Lastly, we performed a refinement in which all ligand valence parameters for the three crystallographically distinct ammonia molecules were constrained to be equal (CVD1), another in which the valence parameters for the thiocyanate groups were constrained to be equal (CVD2), and a further one in which the parameters for both the ammonia molecules and the thiocyanate groups were constrained (CVD3) to be the same. The results of the seven refinements, spherical free atom, no diffuse functions (S), valence-orbital population model, no diffuse functions (V) and with diffuse functions (VD), multipole-charge model, with diffuse functions (MD) and valence-orbital population model, with diffuse functions (CVD1, CVD2 and CVD3), are given in Table 2. Atomic coordinates and equivalent isotropic displacement parameters obtained from refinement MD are given in Table 3, with bonded interatomic distances and angles in Table 4.

Table 1 Experimental details and crystal data

Compound	$[Ru(ND_3)_6][SCN]_3$
T/K	92
M_r	395.4
Diffractometer	Nicolet $P3$
Space group	$C2/c$
a/pm	1353.0(1)
b/pm	927.9(1)
c/pm	1173.8(1)
β/°	104.10(1)
U/nm^3	1.4292(4)
Z	4
F(000)	760.6
μ_{Mo}/mm^{-1}	1.485
Crystal morphology	{100} and {−111}
Maximum dimensions/mm	0.25
Total data	35 711
Unique data	7531
Data with $I > 3\sigma(I)$	5570
$2\theta_{max}$/°	100.3
Merging $R(I)$	0.0228
$\Sigma\sigma(I)/\Sigma I$	0.0169
Maximum, minimum h,k,l	−29,29; −20, 20; −24,24
Radiation	Graphite-monochromated Mo-Kα (λ = 710.069 pm)
Collection mode	ω–2θ
Maximum, minimum analytic absorption correction	0.583, 0.701
No. of standards, every 100	6
Mean standards decay (%)	1 in 21 d

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Discussion

Geometry and Atomic Displacements.—The lower temperature, the deuteriation, the more extensive data, and improved modelling combine to decrease the estimated standard deviations (e.s.d.s) of the structural parameters by a factor of approximately three over the 295 K data[5] results. The structure has been fully discussed elsewhere.[5,14] The $Ru(ND_3)_6$ fragments are bonded to the thiocyanate fragments through approximately linear N–D ··· N and N–D ··· S contacts, as shown in Table 5. The increased accuracy here shows that the RuN_6 fragment is not quite octahedral in stereochemistry. The much improved hydrogen-site positional accuracy confirms the low-symmetry $Ru(ND_3)_6$ conformation with no approximate symmetry elements save the crystallographically required inversion centre.[13] The $Ru(ND_3)_6$ conformations in various crystals are further discussed in ref. 14.

For harmonic thermal motion, neglecting zero-point effects, we might expect the displacement parameters to decrease by the

Table 2 Refinements * of the charge-density X-ray diffraction data for $[Ru(ND_3)_6][SCN]_3$

	S	V	VD	MD	CVD1	CVD2	CVD3
No. of parameters	232	297	313	355	290	297	275
No. of valence parameters	0	65	81	123	58	65	43
$R(I)$ (%)	2.77	2.19	1.78	1.70	1.92	1.89	1.92
$R'(I)$ (%)	4.27	3.64	3.27	3.18	3.36	3.34	3.37
χ^2	1.26	1.16	0.94	0.88	0.98	0.98	0.98
$R(F)[I > 3\sigma(I)]$ (%)	1.88	1.69	1.55	1.50	1.59	1.58	1.59

* See text for definitions.

Table 3 Positional and equivalent isotropic thermal displacement parameters for $[Ru(ND_3)_6][SCN]_3$

Atom	X/a	Y/b	Z/c	U_{eq} [a]/pm^2
Ru	$\frac{1}{4}$	$\frac{1}{4}$	0	160
S(1)	0.081 73(3)	0.313 74(3)	0.420 2(1)	280
C(1)	0.124 0(2)	0.349 6(2)	0.560 9(6)	255
N(1)	0.154 7(1)	0.377 9(2)	0.660 6(4)	343
N(11)	0.196 1(2)	0.295 0(3)	0.151 3(3)	243
N(12)	0.196 9(2)	0.036 2(2)	0.001 8(3)	223
N(13)	0.108 1(1)	0.314 9(2)	−0.105 4(2)	215
S(2) [b]	−0.072 3(1)	−0.030 1(1)	0.292 0(1)	196
C(2) [b]	0.024 9(6)	−0.006 1(3)	0.244 1(4)	177
N(2) [b]	0.100 5(6)	0.001 0(8)	0.208 5(4)	404
D(111)	−0.228(1)	0.248(2)	0.290(2)	311(67)
D(112)	0.195(1)	0.383(3)	0.331(1)	299(55)
D(113)	−0.138(3)	0.269(2)	0.359(1)	542(68)
D(121)	−0.152(2)	0.030(2)	0.468(2)	910(82)
D(122)	−0.244(1)	−0.029(2)	0.459(1)	186(54)
D(123)	0.176(1)	0.002(2)	0.429(2)	479(65)
D(131)	0.058(2)	−0.243(2)	0.387(2)	129(62)
D(132)	−0.088(1)	0.401(3)	−0.409(1)	188(59)
D(133)	0.112(1)	−0.328(2)	0.309(2)	114(50)

[a] One-third trace of the anisotropic thermal displacement tensor. [b] Site occupation parameter = 0.5000.

Table 4 Bond lengths (pm) and angles (°) for $[Ru(ND_3)_6][SCN]_3$

Ru–N(11)	211.9(3)	N(11)–D(112)	85(3)
Ru–N(12)	211.1(2)	N(11)–D(113)	81(4)
Ru–N(13)	210.3(2)	N(12)–D(121)	77(3)
S(2)–C(2)	156.7(8)	N(12)–D(122)	92(2)
C(2)–N(2)	119.7(11)	N(12)–D(123)	91(3)
S(1)–C(1)	164.4(6)	N(13)–D(131)	94(2)
C(1)–N(1)	117.3(7)	N(13)–D(132)	87(2)
N(11)–D(111)	84(2)	N(13)–D(133)	103(2)
N(11)–Ru–N(12)	90.6(1)	Ru–N(12)–D(122)	115(1)
N(11)–Ru–N(13)	89.2(1)	Ru–N(12)–D(123)	112(1)
N(12)–Ru–N(13)	89.4(1)	D(121)–N(12)–D(122)	104(2)
S(2)–C(2)–N(2)	174.9(4)	D(121)–N(12)–D(123)	107(2)
S(1)–C(1)–N(1)	178.6(3)	D(122)–N(12)–D(123)	104(2)
Ru–N(11)–D(111)	112(2)	Ru–N(13)–D(131)	113(1)
Ru–N(11)–D(112)	115(1)	Ru–N(13)–D(132)	116(1)
Ru–N(11)–D(113)	110(1)	Ru–N(13)–D(133)	111(1)
D(111)–N(11)–D(112)	110(2)	D(131)–N(13)–D(132)	114(2)
D(111)–N(11)–D(113)	105(2)	D(131)–N(13)–D(133)	101(2)
D(112)–N(11)–D(113)	105(2)	D(132)–N(13)–D(133)	100(2)
Ru–N(12)–D(121)	112(1)		

Table 5 Short intermolecular contact distances (pm) and angles (°) for $[Ru(ND_3)_6][SCN]_3$

D(111) ··· N(1)	224(2)	D(123) ··· S(2)	264(2)
D(112) ··· N(1)	228(3)	D(123) ··· N(2)	254(3)
D(113) ··· N(2)	270(2)	D(131) ··· S(2)	270(2)
D(121) ··· N(2)	236(3)	D(132) ··· S(1)	266(2)
D(121) ··· S(2)	262(3)	D(133) ··· N(1)	202(2)
D(122) ··· S(1)	271(2)		
N(11)–D(111) ··· N(1)	164(2)	N(12)–D(123) ··· S(2)	149(1)
N(11)–D(112) ··· N(1)	162(1)	N(12)–D(123) ··· N(2)	157(2)
N(11)–D(113) ··· N(2)	119(2)	N(13)–D(131) ··· S(2)	160(2)
N(12)–D(121) ··· N(2)	148(2)	N(13)–D(132) ··· S(1)	159(2)
N(12)–D(121) ··· S(2)	154(2)	N(13)–D(133) ··· N(1)	165(1)
N(12)–D(122) ··· S(1)	156(2)		

ratio of the temperatures, a factor of 92/295 = 0.3, on decrease in the experimental temperature from 295 to 92 K. In other systems we have observed such factors.[5–9] Here, however, the decrease is only of between 0.4 and 0.5 in the *a* and *b* directions, and between 0.6 and 0.7 in the *c* direction for the non-hydrogen atoms. This indicates that, particularly along *c*, the displacement factors reflect some static disorder, not just thermal motion. This is also reflected in the fact that *c* is almost independent of temperature, while *a* and *b* contract noticeably between 295 and 92 K. Anharmonic-displacement parameters are significant for all the non-hydrogen atoms. The size of these anharmonic parameters make visual interpretation of deformation-density maps difficult. In the model we have four types of adjustable parameters: they are (*i*) the purely experimental ones, such as the scale factor, (*ii*) the valence-orbital population, (*iii*) the harmonic atomic-displacement and (*iv*) the anharmonic atomic-displacement parameters. The latter three types are relatively uncorrelated with each other since they are most important at respectively low, medium and high values of $(\sin\theta)/\lambda$. In view of the deliberate flexibility of this parameter set, it is not surprising that the data can be fitted well. However, the usual caveat of such a model-dependent approach must be emphasised: the good fit does not confirm the physical reality of the values obtained for the parameters. For example, it is well known that the thermal atomic-displacement tensor, *U*, subsumes inelastic-scattering effects. We may compare the present result with the case of the ammonium–copper Tutton salt[11] where an underlying hole in the $3d_{x^2-y^2}$ orbital is completely obscured by anharmonic effects at 85, but not at 9 K.[9,10] However, in that case a treatment which includes anharmonicity still reveals the 9 K valence-charge density in the least-squares analysis even at 85 K. It appears that, to current accuracy, the valence-charge density is not, in this model, temperature dependent and does not subsume other temperature-dependent effects.

Charge Density.—(*a*) *Ruthenium* 4d *populations and the magnetic properties.* The refined values of the ruthenium 4d populations are shown in Table 6. There is σ donation into the 4d e_g orbitals of 0.65(7) e. The t_{2g} population of 4.91(7) e is little changed from the free Ru^{III} value of 5.0 e. Because of the absence of π orbitals on N, we expect the co-ordinated ammonia molecules to be σ donors, but, in a first approximation at any rate, neither π donating or accepting. The present analysis supports this supposition which is based on indirect, spectroscopic, experiments. For the t_{2g} orbitals we have close to a single electron hole. The experimental refinements all show that this is distributed almost equally over the $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals. The $\langle xy/yz\rangle$ and $\langle x^2 - y^2/z^2\rangle$ mixing parameters, which describe the orientation of the t_{2g} orbital quantization axes, are less stable, and change from refinement to refinement. After taking possible systematic errors into account, we cannot say whether their values are significant.

In this case, a rhombic ligand-field model, with axes aligned close to the Ru–N octahedron axes provides a very good description of single crystal, ESR and magnetisation data.[5] This model also predicts the distribution in the charge density amongst the t_{2g} orbitals, given an initial assumption of five t_{2g} electrons. The only significant contribution is from the ground state since the first excited state is calculated to lie 1431 cm^{-1} above the ground state, and so cannot be significantly thermally populated. The model predicts the populations shown in Table 6. These populations are almost isotropic because the spin-orbit coupling constant of 1000 cm^{-1} is much larger than the energy differences within the t_{2g} orbital set, of -340 and -170 cm^{-1}.

The agreement with this experiment is good for the t_{2g} orbitals. The substantial magnetic anisotropy observed does not appear, either experimentally or theoretically, in the charge density. Both are close to cubic in symmetry. The differences in the theoretical populations, reflecting anisotropy of the ligand field, are a little too small to show in the experiment here, given the size of the e.s.d.s. However, lowering the temperature from 85 to 9 K for the ammonium–copper Tutton salt halved the e.s.d.s. If that were repeated here the ligand-field-induced differences would become detectable. The e_g populations are significantly greater in the experiment, reflecting covalence which is not taken into account in the ligand-field model. The magnetic properties associated with the spin in the t_{2g} orbitals are insensitive to these populations. The ligand-field model is not useful in predicting them, as it only deals with anisotropy in t_{2g} populations.

The e.s.d.s for the ruthenium atom 4d populations are comparable to those obtained at similar temperatures with first-row transition metals (see, for example, ref. 9), although not as good as those from a very low temperature study.[10] The extra uncertainty introduced by subtracting a much larger core density for a second-row metal is evidently not of as much importance as had been anticipated. By contrast, the 5p populations are not at a worthwhile level of significance, whereas those for 4p in the first series appear to be defined to at least some extent. We obtain here $5p_x = 0.2(4)$, $5p_y = 0.4(4)$ and $5p_z = 1.1(4)$ e.

(*b*) *Intermolecular effects.* In order to describe adequately the total charge density in the complex it is necessary to introduce additional diffuse functions on the nitrogen, carbon, and sulfur atoms. There is a significant improvement in fit between refinements V and VD, as seen in Table 2. However these diffuse functions make a decomposition of the total density into fragments even less meaningful than in usual charge-density analysis practice. There may now be substantial overlap of functions centred on different atoms. In particular, for 'short' intermolecular interaction distances we may perhaps expect that 'charge transfer' may have a reduced effect on agreement factors and so be less well defined. This charge-density analogue of the basis-set superposition error of quantum chemistry has recently been explored in the case of K_2BeF_4.[15] We must remember that we are estimating only certain Fourier components of the time-average crystal charge density. This is the observable quantity, and it is what must be calculated theoretically, perhaps by the *ab initio* methods of theoretical chemistry.[16,17] However that is a difficult, and as yet not clearly defined process. Meanwhile, although arbitrary and open to different interpretations, the parameters of particular empirical models may suggest what factors must be incorporated in any more satisfactory theoretical calculations. For example, the question of whether a calculation which incorporates a proper treatment of the periodicity at the crystal lattice is necessary, or whether examination of a few units in a cluster will do, may be addressed within the present limits of experimental accuracy.

The total model charge on the $Ru(ND_3)_6$ fragment is 1.77, on S(1)–C(1)–N(1) -0.37 and on S(2)–C(2)–N(2) -1.01 e. To test if the difference between the thiocyanate groups is real we must perform further refinements. This is because, as for K_2BeF_4, parameter correlation may be severe, and may not be obvious in a simple correlation matrix. We find that if either the thiocyanate group parameters on the one hand or the ammonia molecular valence parameters on the other hand are all constrained to be equal there is substantial degradation in the fit. However, if both sets are constrained simultaneously, the further degradation in fit is minimal. This implies that, by the latter constraint, we are suppressing differential charge transfers from the thiocyanate ions to the ammonia molecules. The lower charge of S(1)–C(1)–N(1) compared to S(2)–C(2)–N(2) is not only real, but is due to 'intermolecular' transfer to particular ammonia molecules.

Although it cannot be a rigorous comparison because of differences in the definition of overlap and atom-centred populations, we may compare the populations with the results of a local-density functional *ab initio* theoretical calculation for the thiocyanate ion whose results are set out in Table 7. The calculated and experimental results for S(2)–C(2)–N(2) agree fairly well, and reinforce the belief that S(2)–C(2)–N(2) is relatively unaffected by bonding. However, S(1)–C(1)–N(1) has a quite different charge distribution. If we compare the charge distribution on S(1)–C(1)–N(1) with that on S(2)–C(2)–N(2), we see that the former, compared to the latter, has lost electrons from the sulfur and nitrogen atoms. The atom C(1), by contrast, has gained electrons relative to C(2). Beside this loss of overall charge, the distribution is markedly polarised, with the charge transferred from both ends to the middle of the molecule. It seems likely that these effects for S(1)–C(1)–N(1) are to be associated with the much shorter hydrogen bond contacts to N(1), relative to those to N(2). From Table 5, the average of such lengths is 218 (with a particularly short 202 member) *versus* 253 pm for S(2)–C(2)–N(2).

On the $Ru(ND_3)_6$ fragment, the charge on the $N(11)D_3$ molecule is 0.10, on $N(12)D_3$ 0.69 and on $N(13)D_3$ -0.56 e. From previous experience we expect net positive charges on each amine in a free $[Ru(ND_3)_6]^{3+}$ ion of some few tenths of an electron due to the σ donation onto the ruthenium atom. The negative charge on the $N(13)D_3$ molecule appears surprising. However, if we again look at the hydrogen-bond contacts (Table 5) we see that $N(13)D_3$ is linked to the thiocyanate N(1) by the particularly short 202 pm distance, $N(11)D_3$ is linked by two hydrogen bonds of 224 and 228 pm and $N(12)D_3$ only

Table 6 4d population parameters (e) obtained from refinement VD compared with ligand-field model predictions for $[Ru(ND_3)_6][SCN]_3$

Angular type	Observed	Predicted
$\langle xy/xy\rangle$	1.61(5)	1.59
$\langle xz/xz\rangle$	1.63(5)	1.67
$\langle yz/yz\rangle$	1.67(5)	1.74
$\langle x^2 - y^2/x^2 - y^2\rangle$	0.35(6)	—
$\langle z^2/z^2\rangle$	0.31(5)	—
$\langle z^2/x^2 - y^2\rangle$	−0.56(8)	—
$\langle xy/yz\rangle$	−0.61(7)	0
$\langle xy/xz\rangle$	−0.20(6)	0
$\langle xz/yz\rangle$	0.03(6)	0

Table 7 Atomic and overlap populations (e) on the thiocyanate ions in $[Ru(ND_3)_6][SCN]_3$

	DV-Xα Theory*			S(2)–C(2)–N(2)			S(1)–C(1)–N(1)		
	S	C	N	S	C	N	S	C	N
S	5.72	1.16	−0.13	6.36	0.44	0.00	5.20	0.00	0.0
C	—	2.81	1.14	—	2.38	1.31	—	5.20	0.1
N	—	—	5.31	—	—	5.50	—	—	4.8

DV-Xα numerical local-density functional calculations with experimental bond lengths (ref. 3); 1500 points, basis set 1s–4f, potential fit to 1 = 2 multipoles, for S, C and N.

has 236 and 254 pm contacts. Thus a hypothesis that there is a substantial charge transfer through the 202 pm bond to N(13)D_3 from S(1)–C(1)–N(1) is supported, with less transfer to N(11)D_3, and even less to N(12)D_3. If we look at hydrogen 1s populations we find the lowest population is for D(133) [0.67(4) e], which is involved in the shortest contact. There is a noticeable, although somewhat irregular trend, that the D 1s population increases as the D ··· N or D ··· S distances increase. There is the inverse trend in the apparent N–D bond lengths, with N(13)–D(133) longest, shortening as the 'intermolecular' contact distances increase. A neutron-diffraction structure, which would give the true hydrogen nuclear positions, would be required before a more detailed analysis of these 'intermolecular' influences is warranted.

Given the possible significant overlaps, for example of hydrogen 1s and nitrogen diffuse functions, the individual fragment charges should not be taken literally. However, we can conclude that in this crystal we observe that as contact distances from N–D to NCS (or SCN when appropriate) decrease, substantial charge is transferred from SCN to ND_3, and that in addition the ND_3 unit becomes more polarised, with charge migrating from D to N, while the SCN group is also polarised by charge migration towards its centre. Such an intermolecular charge transfer has not been explicitly demonstrated previously in a transition-metal complex crystal. In earlier diffraction studies this has relied on indirect evidence, for example, the different charge density of $Cr(CN)_6$ units in $Cs_2K[Cr(CN)_6]$[18] and in $[Co(ND_3)_5(D_2O)][Cr(CN)_6]$[19] and the observation of spin transfer to the hexaamminecobalt(III) fragment in the latter case.[20] Other techniques, such as vibrational spectroscopy, should also be sensitive to charge flows of the size apparent here.

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