Nitrogen-14 Nuclear Quadrupole Resonance Study of Bonding in Transition-metal Cyanides

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Nitrogen-14 n.q.r. frequencies were measured for $K_4[Mo(CN)_8]\cdot2H_2O$, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]\cdot3H_2O$, $Ba_2[Fe(CN)_6]\cdot3H_2O$, $K_4[Ru(CN)_6]\cdot3H_2O$, $K_2[Ni(CN)_4]$, $Na_2[Ni(CN)_4]$, $K_2[Pd(CN)_4]$, $Na_2[Pd(CN)_4]$, $K[Ag(CN)_2]$, and $K[Au(CN)_2]$ at 77 K. Two sets of cyanides with different σ- but equal π-orbital populations were found in $K_4[Mo(CN)_8]\cdot2H_2O$. Changing from Mn to Co in hexacyanides produced an increase in back bonding and a decrease in σ bonding. In the nickel to platinum group cyanides no back bonding was found and the changes in the principal quantum number produced variations only in the nitrogen σ population. In the zinc to mercury group cyanides almost no change was found with variation of the principal quantum number in either σ or π populations. In dicyanides of Hg, Ag, and Au, back bonding increased in that order. It was found also that the variations in the metal charge caused important modifications in the population of the σ and π orbitals of the -CN group.

Two interesting features of the chemistry of the 3*d*, 4*d*, and 5*d* transition-metal cyanides are the existence of many metals in low oxidation states and the wide range in metal to ligand ratio, spanning an unusually large variety of stereochemical configurations.[1,2] Also, the stabilization of low oxidation states has been interpreted as a result of the ability of the CN^- to accept metal-ion *d* electrons in its two π* orbitals.[1,2] In order to obtain further information about bonding in the transition-metal cyanides, we have determined the ^{14}N nuclear quadrupole resonance[3,4] (n.q.r.) spectrum of $K_4[Mo(CN)_8]\cdot2H_2O$, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]\cdot3H_2O$, $Ba_2[Fe(CN)_6]\cdot3H_2O$, $K_4[Ru(CN)_6]\cdot3H_2O$, $K_2[Ni(CN)_4]$, $Na_2[Ni(CN)_4]$, $K_2[Pd(CN)_4]$, $Na_2[Pd(CN)_4]$, $K[Ag(CN)_2]$, and $K[Au(CN)_2]$ at 77 K. Our data, together with those available[5–7] for other transition-metal cyanides were interpreted by means of the Townes and Dailey theory[3,4] and the results discussed in terms of the co-ordination bond present in those cyanides.[1,2]

Experimental

Nitrogen-14 n.q.r. spectra were obtained at 77 K using a Nicolet-Matec FT pulse spectrometer. Observed frequencies were estimated to be accurate within ±100 Hz except for $K_3[Fe(CN)_6]$ and $K[Au(CN)_2]$ where the accuracy was ±300 Hz and ±1 kHz, respectively, due to the broad lines found with these cyanides. Some of the transition-metal cyanides were commercially available and they were used without further purification; the majority were produced following standard procedures.[1,2] All cyanides gave satisfactory elemental analyses.

Results

For ^{14}N ($I = 1$), the n.q.r. spectrum of an independent site consists, in general, of three lines:[3,4] ν^+, ν^-, and ν^d. From the resonance frequencies, we obtain the nuclear quadrupole coupling constant (n.q.c.c.), e^2qQ/h, and the electric field gradient (e.f.g.) asymmetry parameters,[3,4] η. For a vanishing η, we have a single frequency ν^0. Table 1 shows the resonance frequencies measured for several transition-metal cyanides at 77 K.

For $K_4[Mo(CN)_8]\cdot2H_2O$, we detected eight lines, thus showing the existence of four non-equivalent N sites. The N sites were divided into two noticeably different sets as seen in Table 1. The results obtained for the octacyanomolybdate did not agree with *X*-ray data which showed six non-equivalent sites at room temperature.[8,9] This result suggests that a phase transition may exist between 77 K and room temperature for this complex. The spectrum of the octacyanomolybdate could be interpreted either as being produced by the CN^- groups of a single octacyanomolybdate ion which are divided into two distinct but equally populated sets, or by CN^- groups of two octacyanomolybdate ions occupying strongly non-equivalent positions within the unit cell. The last case seems unlikely because the difference between the two hypothetically non-equivalent ions is much larger than the typical changes in frequency found for non-equivalent sets of CN^- groups in cyanides of known structure.[5,7] Consequently, the non-equivalence of the cyanides in $K_4[Mo(CN)_8]\cdot2H_2O$ seems to be of intramolecular origin and reflects differences in metal ion to ligand bonding.

Four ν^+ and four ν^- lines were found for the low-temperature phase of the simple monoclinic polytype[10] of $K_3[Fe(CN)_6]$ at 77 K. The lines were weak, broad (2—3 kHz), and some showed overlap as seen in the Figure. The spectrum of potassium hexacyanoferrate(III) is not compatible with the crystal structure determined[10] at 95 K, since n.q.r. showed four N sites while only three sites were found from the *X*-ray data. Further work is in progress in order to clarify this point.

We obtained, for $K_4[Fe(CN)_6]\cdot3H_2O$ and for the isostructural $K_4[Ru(CN)_6]\cdot3H_2O$, a low-frequency quartet formed by two ν^+ and two ν^- lines, and an upper quartet of equivalent composition. The only known phase transition of potassium hexacyanoferrate(II) produces a change in orientation of the water molecules within the unit cell, whilst maintaining all the other atoms without significant changes.[11,12] The spectrum obtained at 77 K was compatible with such a change as its multiplicity agreed with the number of N sites found at room temperature.[11,12] We found a ν^+ and a ν^- line for $Ba_2[Fe(CN)_6]\cdot3H_2O$, thus showing the existence of only one N site. For $Na_2[Ni(CN)_4]$, $Na_2[Pd(CN)_4]$, and $K_2[Pd(CN)_4]$ a pair of ν^+ and a pair of ν^- lines were obtained showing the existence of two N sites in such complexes. Unfortunately, we

Table 1. ^{14}N N.q.r. frequencies, nuclear quadrupole coupling constants, e^2qQ/h, and asymmetry parameters, η

Compound	ν^-/kHz	ν^+/kHz	e^2qQ/h (kHz)	η
$K_4[Mo(CN)_8]\cdot 2H_2O$	2 567.2	2 666.2	3 493	0.050
	2 569.2	2 676.0		
	2 755.8	2 861.3	3 741	0.056
	2 759.7	2 864.7		
$K_3[Mn(CN)_6]$	2 843.6	2 975.1	3 909	0.061
	2 872.0	2 984.4		
	2 881.4	2 994.3		
	2 888.8	3 009.6		
$K_3[Fe(CN)_6]$	2 797.9	2 870.0	3 790	0.036
	2 806.1	2 874.1		
	2 812.5	2 879.8		
	2 815.2	2 883.1		
$K_3[Co(CN)_6]$*	2 688.8	2 787.8	3 661	0.049
	2 706.3	2 789.2		
	2 709.9	2 794.5		
$K_4[Fe(CN)_6]\cdot 3H_2O$	2 498.0	2 528.4	3 352	0.019
	2 498.9	2 529.5		
	2 541.8	2 575.1	3 425	0.023
	2 556.2	2 601.5		
$Ba_2[Fe(CN)_6]\cdot 3H_2O$	2 471.6	2 570.9	3 362	0.059
$K_4[Ru(CN)_6]\cdot 3H_2O$	2 571.2	2 624.7	3 491	0.032
	2 580.5	2 633.4		
	2 596.1	2 649.0		
	2 613.5	2 674.0		
$K_2[Zn(CN)_4]$*		3 104.2	4 139	0
$K_2[Cd(CN)_4]$*		3 149.1	4 198	0
$K_2[Hg(CN)_4]$*		3 035.6	4 048	0
	3 041.4	3 069.4	4 074	0.014
$K_3[Cu(CN)_4]$*	2 943.8	3 002.1	3 964	0.029
$K_2[Ni(CN)_4]$	2 921.7	2 955.4	3 918	0.017
$Na_2[Ni(CN)_4]$	2 879.1	2 907.0	3 858	0.016
	2 876.7	2 910.9		
$K_2[Pd(CN)_4]$	2 612.8	2 724.0	3 575	0.058
	2 646.0	2 740.0		
$Na_2[Pd(CN)_4]$	2 666.6	2 789.4	3 652	0.061
	2 699.8	2 801.2		
$K_2[Pt(CN)_4]\cdot 3H_2O$*	2 549.7	2 614.2	3 467	0.032
	2 594.7	2 641.2		
$K[Cu(CN)_2]$*	2 965.8	3 138.2	4 069	0.085
	2 394.7	2 525.3	3 280	0.080
$K[Ag(CN)_2]$		2 928.8	3 905	0
$K[Au(CN)_2]$	2 732 ± 1	2 762 ± 1	3 662	0.016
$[Hg(CN)_2]$*	2 932.5	2 994.8	3 952	0.031

* Data from ref. 5.

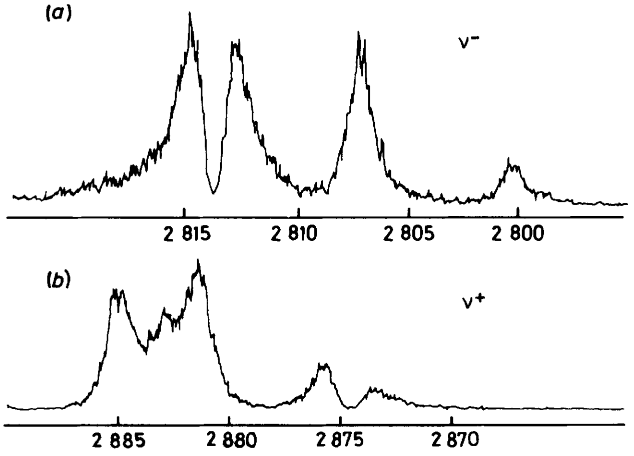

Figure. ^{14}N N.q.r. spectrum of the low-temperature phase of the simple monoclinic structure of $K_3[Fe(CN)_6]$ at 77 K. The accumulation time was 4 h and the number of scans was 720. The irradiation frequency of spectrum (*a*) was 2 825.0 and that of (*b*) was 2 890.0 kHz

could not find a reported crystal structure of any of these cyanides for comparison.

A ν^+ line and ν^- line were found for $K_2[Ni(CN)_4]$ showing the existence of only a single N site. However, the structure at room temperature[13] for such nickel cyanides shows the existence of two N sites indicating the possible occurrence of a phase transition between 77 K and room temperature.

A ν^0 line for $K[Ag(CN)_2]$ and a ν^+ and a ν^- line for $K[Au(CN)_2]$ were found showing that in both cyanides, which are isostructural, there is only one N site. These results are compatible with the structures determined at room temperature.[14]

Discussion

The ground state[2] of the CN^- ion is described as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$. Overlap of the 5σ orbital with *nd*, $(n + 1)s$, and $(n + 1)p$ metal-ion orbitals constitutes the normal metal ion to CN^- σ bond.[15] Also, π bonds may be formed by the overlap of occupied *d* orbitals of the metal ion and the two $2\pi^*$ orbitals of the cyanide ion.[15] The formation of the metal ion to cyanide σ bond reduces the population of the 5σ orbital. As this orbital has a slight antibonding character with respect to the N–C σ bond, donation of some of its population produces an increase in the strength of the N–C σ bond.[15] As a result of efficient metal ion to ligand σ bonding, the C atom becomes more electronegative and therefore more receptive to the metal-ion *d* electrons[1,2,16] that form π bonds.

In order to study the effect of metal-ion co-ordination on the CN^- charge distribution, we have used the Townes and Dailey theory[3,4] in the analysis of the n.q.r. data. For N in a –CN group, we have[17] equations (1) and (2), where l, b, π_x, and π_y

$$\alpha = e^2qQ/e^2q_0Q = l\beta^2 + (1 - \beta^2)b - (\pi_x + \pi_y)/2 \quad (1)$$

$$\alpha\eta = 3(\pi_x - \pi_y)/2 \quad (2)$$

are the populations of the N lone pair, σ, and π orbitals, respectively. We have taken e^2q_0Q/h, the n.q.c.c. for one $2p$ electron in the N atom,[4,5] as 10 MHz. The amount of *s* character of an *sp* bond,[4,5] β, was taken as $\beta^2 = 0.5$. Table 1 shows that there are no indications of co-ordination through the N lone pair because such interaction lowers[7] the nitrogen n.q.c.c. to 3.2 MHz or less. As the observed n.q.c.c.s are all equal or higher than 3.35 MHz, we assume that the N lone pair is not perturbed and set $l = 2$. Equations (1) and (2) now contain three unknowns while n.q.r. only provides two independent pieces of information: e^2qQ/h and η. We have then to choose between setting b or one of the π-orbital populations using values obtained from other sources and solving equations (1) and (2)

Table 2. Populations of nitrogen σ and π_x orbitals

Compound		Population (e)	
		b	π_x
$K_4[Mo(CN)_8]\cdot 2H_2O$	Site A	1.112	1.214
	Site B	1.163	1.214
$K_2[Zn(CN)_4]$		1.228	1.200
$K_2[Cd(CN)_4]$		1.240	1.200
$K_2[Hg(CN)_4]$		1.219	1.204
		1.209	1.200
$K_3[Cu(CN)_4]$		1.201	1.208
$K_2[Ni(CN)_4]$		1.188	1.204
$Na_2[Ni(CN)_4]$		1.176	1.204
$K_2[Pd(CN)_4]$		1.129	1.214
$Na_2[Pd(CN)_4]$		1.145	1.215
$K_2[Pt(CN)_4]\cdot 3H_2O$		1.100	1.207

* Values calculated from average frequencies as in ref. 5.

for the remaining two unknowns, or interpreting the variations directly in terms of the differences in population of the N orbitals.

The symmetry of the metal-ion orbitals, and the spatial arrangement plus the orbitals of the ligands determine the occurrence of multiple bonding between CN^- and the metal ion.[18] Group theory[18,19] provides information about multiple bonding in this type of complex; thus allowing us to determine the correct approach to equations (1) and (2). For octacyanides, there is only one π bond between the metal ion and the CN^- group.[19] We assume that in such cases one of the orbitals of the CN^- group is not perturbed and so set its population equal to 1.200 e, as in benzonitriles.[17] In the tetracyanides there exists the possibility of weak secondary π interactions.[19] As the degree of π bonding in such cyanides is low,[15] we could neglect such interactions and proceed as for the octacyanide.

Table 2 shows the results for the σ and π populations obtained for octacyanide and tetracyanides. The most interesting features for the tetracyanides are the small changes in the π-orbital population and the relatively large variations in the σ-orbital population when the metal ion is changed. The formation of a metal ion to carbon σ bond will produce an increase in strength of the N–C bond[15] which in turn originates a decrease in b as part of the nitrogen σ population moves towards the interatomic region.[16] Thus, the results shown in Table 2 indicate that the main effect of changing the metal ion in these cyanides is concentrated in the N–C σ bond with only a marginal change in back bonding.

The octacyanomolybdate ion has a dodecahedral structure[8] in $K_4[Mo(CN)_8]\cdot 2H_2O$ at room temperature. Hoffman and coworkers[20] found that the dodecahedral geometry is the most stable for ML_8 ions with d^2 metals, and that the ligands are equally divided into two sets, labelled A and B, with B having the strongest metal ion to ligand σ and π bonds. The n.q.r. spectrum of potassium octacyanomolybdate confirms the existence of two widely different sets of CN^- ions. On the other hand, the π bonding in dodecahedral ions of this type is produced by a $d_{x^2-y^2}$ orbital which interacts with suitable orbitals of the ligands.[20] Because the spatial distribution of this d orbital allows interactions with only one of the orbitals of the cyanides, we then expect that the B sites will have a larger π population than the A sites. Table 2 shows that this not the case in potassium octacyanomolybdate because the π_x values for both sets of CN^- ions are the same. Orgel[21] has predicted that π-acceptor ligands should enter B sites in this type of ML_8 ion due to their better π-bonding capabilities. Table 2 also shows that this is not the case for $K_4[Mo(CN)_8]\cdot 2H_2O$.

On the other hand, the changes in n.q.c.c. and η for the hexa- and di-cyanides must be interpreted directly in terms of the differences between the populations of σ and π orbitals because both π orbitals of each cyanide could interact equally well with the metal-ion d orbitals.[19] We see from equation (1) that in the hexa- and di-cyanides the n.q.c.c.s will be more sensitive to back bonding than in complexes where only one of the cyanide π bonds is involved in such interaction. In trivalent hexacyanides, the C–N σ-bond strength increases with the atomic number because the $3d$ electrons do not screen the metal ion from the CN^- group very well and because the effective nuclear charge of the metal increases in the order[22] Co > Fe > Mn. Also, the back bonding should increase as the number of $3d$ electrons available also increases in the same order.[22] Table 2 shows, as expected, that the n.q.c.c.s decrease as we move from Mn to Co. Such a change could be interpreted as resulting from a decrease in b and/or an increase in the average nitrogen π population. The decrease in n.q.c.c. value as the metal oxidation drops in hexacyanoferrate-(III) and -(II) could be explained as resulting from a decrease in metal-ion to ligand σ-bond strength and an increase in back bonding produced by a higher delocalization[22] of the T_{2g} orbitals in Fe^{II}. Such variations will, on the one hand, increase b as the N–C σ bond is weakened and on the other augment the N π population through larger back bonding. A similar effect was found for the pairs of compounds $K_3[Co(CN)_6]/K_4[Fe(CN)_6]$, $K_2[Zn(CN)_4]/K_3[Cu(CN)_4]$, and $K[Au(CN)_2]/[Hg(CN)_2]$.

The changes in populations calculated by means of the Townes-Dailey theory for first-row transition-metal hexacyanides are in agreement with those obtained by *ab initio* molecular orbital (m.o.) calculations.[23] The agreement between the calculation performed for the isolated ions[23] and the n.q.r. results obtained in the solid state shows that the contributions of the crystal field are small in these cyanides. This result is confirmed by the small changes found in the n.q.r. spectrum of the Ba and K salts of the hexacyanoferrate(II) ion.

The n.q.c.c. of the Ru^{II} is higher than that of the Fe^{II} hexacyanide showing that the increase in the principal quantum number produces an increase in b and/or a decrease in back bonding. This result shows the same trend found by others[24] in transition-metal hexachlorides and may be related to the changes in metal-ion size and its effect on the ligand coordination.[22]

In tetracyanides, as we move down the nickel to platinum group, the n.q.c.c.s decrease, while in the zinc to mercury group they show little variation. These changes may be interpreted as resulting from an increase in back bonding and/or a decrease in b resulting from a stronger σ bonding when going from the zinc to the nickel group. The source of that difference could be found in the metal-ion hybridization, *i.e.* sp^3 for zinc and dsp^2 for the nickel group[19] cyanides. In the latter case, the inclusion of the d orbital will increase covalency and thus augment the ligand to metal-ion donation with respect to the zinc group and will produce lower n.q.c.c.s as observed.[16]

An *ab initio* m.o. calculation[25] performed for $[Ni(CN)_4]^{2-}$ showed that the metal ion to ligand bond lacked any significant back bonding. The value of π_x found in $K_2[Ni(CN)_4]$ confirms the m.o. results[25,26] because it is very close to the unperturbed value of 1.200 e. The values of the π population and its constancy throughout the nickel group shows that back bonding is very small in these cyanides. Table 1 shows that the substitution of K by Na in the tetracyanides of Ni and Pd has little effect on the η values but changes the n.q.c.c.s in a rather irregular way. Unfortunately, the crystal structure of these tetracyanides is not known and hence we cannot proceed with our analysis until that information becomes available.

On the other hand, Jones and Swanson[27] from the presence of a weak Zn–CN directional force constant concluded that back bonding was absent in $K_2[Zn(CN)_4]$. Table 2 shows that the population obtained for the zinc tetracyanide is very close to

1.200 e, confirming this result.[27] The π population found in the other tetracyanides indicates that there is little or no back bonding in the cyanides of the zinc group.

The analysis of the copper to gold group dicyanides is complicated because the co-ordination number of the metal ion is three and the complex ion has a helical structure[28] in $K[Cu(CN)_2]$, while in the other dicyanides the complex ions are linear with a two-co-ordinate metal ion.[14] However, we could proceed with our analysis if we take the n.q.r. data of the mono-co-ordinated[7] CN^- present in the copper cyanide as representative of a hypothetical two-co-ordinate complex. Table 1 shows that an increase in the principal quantum number lowers the n.q.c.c. values of the copper group dicyanides while the η values show a minimum for Ag. The relatively high value of η found for the copper dicyanide could be attributed to the asymmetric interaction of the π and the *d* orbitals produced by the non-linearity of the NC–Cu–CN bonds.[16] The decrease in n.q.c.c.s in the copper group is similar to that found in the nickel group tetracyanides indicating that the changes in principal quantum number play a similar role in both sets of complexes.

Jones[29] found that there is little back bonding in $[Hg(CN)_2]$ and that back bonding increases in the order Au > Ag > Hg. Table 1 shows that the n.q.c.c.s decrease as we move from Hg to Au. This trend may be interpreted as indicating that the increase in the π population observed by Jones[29] is larger than the changes expected in *b* for this group of cyanides.

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