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Studies in Transition-metal Cyano Complexes.
Part V*. Vibrational and ^{13}C NMR Spectroscopic Data on Pentacyano Complexes, and the X-ray Crystal Structure of $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$

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Abstract

Raman, infrared and ^{13}C NMR data are presented for a series of pentacyano complexes $[MH(CN)_5]^{3-}$ (M = Co, Rh, Ir); $[RhX(CN)_5]^{3-}$ and $[PtX(CN)_5]^{2-}$ (X = Cl, Br, I); and $[FeX(CN)_5]^{n-}$ (X = NO, CO, PPh_3, $AsPh_3$, NO_2, SO_3, py, NH_3 and DMSO) and Cotton–Kraihanzel force constants calculated. ^{14}N NMR data are also reported for $[RhH(CN)_5]^{3-}$, $[PtCl(CN)_5]^{2-}$ and a number of unsubstituted cyano complexes. Reasons for changes in CN stretching frequencies, CN force constants and ^{13}C chemical shifts are discussed for these and for $[Ru_2N(CN)_{10}]^{5-}$.

The X-ray crystal structure of $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$ has been determined. The crystals are triclinic with $a = 8.757(2)$, $b = 9.121(3)$, $c = 9.444(2)$ Å, $\alpha = 106.81(2)$, $\beta = 106.91(2)^\circ$, $\gamma = 112.52(2)^\circ$, space group $P\bar{1}$, $Z = 1$, and the structure has been refined to $R = 0.064$.

Introduction

A number of papers have dealt with the fundamental vibrations and force-fields of hexacyano molecules [2, 3] and ^{13}C chemical shifts for a number of such species have been measured [4]; there are more limited data on ^{14}N NMR shifts for hexacyano species [5]. There is however little work on substituted cyano complexes, and we present here studies on the Raman, infrared, and ^{13}C spectra of pentacyano complexes $[MX(CN)_5]^{n-}$. We calculate, using the Cotton–Kraihanzel approximation [6] which has been shown to be valid for a wide range of metal pentacarbonyl species [7], approximate force constants for the *cis* and *trans* cyano ligands. Since most of the substituting ligands X in $[MX(CN)_5]^{n-}$ for complexes studied here are π-acceptors, we give also the X-ray crystal structure and similar spectroscopic data on $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$, a complex which we have previously reported [8] and which contains the strongly π-donating nitrido ligand. We also report vibrational and ^{13}C NMR data on a number of other substituted cyano complexes, and ^{14}N NMR data for a variety of cyano complexes.

Results and Discussion

(a) Raman and Infrared Data on Pentacyano Complexes

For complexes of the type $[MX(CN)_5]^{n-}$ of C_{4v} symmetry we expect four CN stretches (ν(CN)) $2A_1 + B_1 + E$; all four should be Raman-active with the A_1 modes being polarised, while three ($2A_1 + E$) should also be infrared active. The data in Table I are derived from Raman and infrared studies on aqueous solutions of the complexes. Unlike metal pentacarbonyl complexes $[MX(CO)_5]^{n-}$ where the ν(CO) wavenumbers lie over a fairly wide range, ν(CN) bands are often close together (owing to relatively small CN–CN interactions; dipole–dipole coupling accounts for the larger CO–CO interactions [9]). Assignment of ν_1 (A_1) and ν_{15} (E) modes is fairly straightforward [10]; the weak infrared band at highest energy corresponds to the intense, polarised Raman band and is assigned to ν_1, the totally symmetric stretching vibration of the *cis* cyano ligands, and likewise the E mode (ν_{15}) is assigned to the strongest infrared band because a large change in dipole moment should accompany this vibration. The B_1 mode (ν_9) is Raman active only and depolarised, appearing as a medium to strong intensity band. The exact position of the axial CN stretch ν_2 is sometimes difficult to establish because of overlapping by other bands. Though some complexes do exhibit a second polarised Raman band in the CN stretching region, only in a few cases it is sufficiently strong for reliable polarisation data to be obtained; in the infrared it is often obscured by the intense E mode. Our assignments for $[Pt(CN)_5X]^{2-}$ (X = Cl, Br, I) are close to those reported for the solids [10].

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TABLE I. Vibrational and ^{13}C NMR Spectra of Pentacyano Complexes

	CN stretching frequencies[a] (cm^{-1})				CN force constants (m dyn/Å)			^{13}C chemical shifts[b] (ppm)	
	ν_1 (A_1)	ν_2 (A_1)	ν_9 (B_1)	ν_{15} (E)	k(*cis*)	k(*trans*)	k_i	δ(*cis*)	δ(*trans*)
$[CoH(CN)_5]^{3-}$ [c]	2127	2110p	2100[d]	$\underline{2097}$	16.87	16.95	0.09		
$[RhH(CN)_5]^{3-}$	2147	2119p	2127	$\underline{2105}$	17.15	17.10	0.11	141.0 (*cis* C, Rh 34.4) (*cis* C, H 5.7)	149.0 (*trans* C, Rh 36.5) (*trans* C, H 56.6)
$[RhCl(CN)_5]^{3-}$	2150	$\underline{2140}$	2154	$\underline{2130}$	17.49	17.44	0.04	140.5 (*cis* C, Rh 35.4)	120.0 (*trans* C, Rh 37.5)
$[RhBr(CN)_5]^{3-}$	2148	$\underline{2137}$	2143	$\underline{2128}$	17.40	17.39	0.05	137.7 (*cis* C, Rh 37.6)	119.2 (*trans* C, Rh 39.3)
$[RhI(CN)_5]^{3-}$	2145	$\underline{2135}$	2140	$\underline{2123}$	17.36	17.33	0.05	135.4 (*cis* C, Rh 38.7)	118.5 (*trans* C, Rh 39.6)
$[IrH(CN)_5]^{3-}$	2152	2117p	2125[d]	$\underline{2110}$	17.19	17.10	0.11	120.0 (*cis* C, H 5.5)	126.0 (*trans* C, H 38.0)
$[Fe(NO)(CN)_5]^{2-}$	2173	2160p	2155	$\underline{2143}$	17.66	17.77	0.08	137.0	135.2
$[Fe(CO)(CN)_5]^{3-}$	2090	$\underline{2089}$	2085	$\underline{2070}$	16.47	16.61	0.05		
$[Fe(PPh_3)(CN)_5]^{3-}$	2087	$\underline{2040}$	2057	$\underline{2030}$	16.03	15.84	0.14	178.9	177.5
$[Fe(AsPh_3)(CN)_5]^{3-}$	2087	$\underline{2040}$	2057	$\underline{2030}$	16.03	15.85	0.21	178.1	177.1
$[Fe(NO_2)(CN)_5]^{4-}$	2089	2068	2064	2060	16.28	16.28	0.08	179.8	177.2
$[Fe(SO)_3)(CN)_5]^{5-}$								180.3	179.5
$[Fepy(CN)_5]^{3-}$								180.2	177.1
$[Fe(NH_3)(CN)_5]^{3-}$	2060	$\underline{2057}$	2055dp	$\underline{2040}$	15.99	16.11	0.05	183.0	181.7
$[Fe(DMSO)(CN)_5]^{3-}$								172.0	169.0
$[Ru_2N(CN)_{10}]^{5-}$	2149	2124	2135	2121	17.31	17.18	0.07	141.9	140.1
$[PtCl(CN)_5]^{2-}$	2205	$\underline{2195}$	2193	$\underline{2187}$	18.31	18.35	0.05	92.7 (*cis* C, Pt 821)	75.3
$[PtBr(CN)_5]^{2-}$	2203	$\underline{2193}$	2192	$\underline{2186}$	18.29	18.31	0.05	89.5 (*cis* C, Pt 830)	74.9
$[PtI(CN)_5]^{2-}$	2201	$\underline{2191}$	2188	$\underline{2181}$	18.22	18.28	0.05	87.3 (*cis* C, Pt 827)	74.2

[a] Infrared frequencies underlined; otherwise Raman data. All data for aqueous solutions. [b] *J* values in parentheses (Hz). [c] Raman data for $[CoH(CN)_5]^{3-}$ from ref. 35. All ν_1 modes were observed to be polarised (p) in the Raman with relative intensity (10); the ν_9 mode was normally of relative intensity (4) in the Raman and depolarised. The IR-active ν_{15} mode was very strong in all cases, and the ν_2 band of weak to moderate intensity in the infrared. [d] Band observed both in Raman and infrared.

Cotton–Kraihanzel force constants

The Cotton–Kraihanzel model was developed for analysing and assigning the infrared-active CO stretching frequencies (ν(CO)) of simple and substituted metal carbonyls $MX_n(CO)_{6-n}$, and depends on the fact that ν(CO) lies at much higher wavenumbers (>1850 cm^{-1}) than all other vibrations (<700 cm^{-1}). Such a situation applies also to ν(CN) in cyano complexes; Turner *et al.* have reported that application of the approximation to metal cyano complexes gave good agreement with general quadratic valence force fields [11]; Jones and Swanson [2] applied the method to simple molecules such as $[Au(CN)_2]^-$ and $Hg(CN)_2$ but used data obtained for solids. Alvarez [12] compared Cotton–Kraihanzel force constants with general valence force-field constants for a number of tetra- and hexacyano [12, 13] and hepta-, octa- [13] and substituted cyano complexes [12, 13] (the latter comprising $[PtX(CN)_5]^{2-}$ and *trans*-$[PtX_2(CN)_4]^{2-}$, X = Cl, Br, I), and concluded that the approximation was valid for these. In Table I we list values for *k*(*cis*) (stretching force constants for the *cis* cyano groups), *k*(*trans*) (stretching force constant for the *trans* cyano group) and k_i, the interaction constant for *cis*-CN ligands *cis* to each other for pentacyano complexes. These were calculated by using the secular equations of Cotton and Kraihanzel [6] using all four frequencies ($\nu_1, \nu_2, \nu_9, \nu_{15}$) with a least-squares procedure to obtain the best fit. As in the Cotton–Kraihanzel treatment for carbonyls, no account is taken of the interactions of ν(CN) modes with other vibrations of the molecule, and the calculations use observed ν(CN) frequencies, without corrections for anharmonicity.

We discuss the data in Section c below.

(b) ^{13}C NMR Data on Pentacyano Complexes

We have already shown that ^{13}C NMR demonstrates the absence of aquation of the *trans* cyano ligand in aqueous solutions of $K_3[MH(CN)_5]$ (M = Rh, Ir) [1, 14] and that it is a useful technique for transition metal cyanide chemistry [15]. As with pentacarbonyl species [16] the direct bonding of carbon to metal should produce large chemical shifts and, if the metal has a nuclear spin, allow measurement of *J*(C, M). Although work has been done on pentacarbonyl species [16], there are relatively few data on pentacyano species, e.g., for $[Re(NO)(CN)_5]^{3-}$ [17], and for $[ML(CN)_5]^{n-}$ (M = Fe, Co; L = nitrogen donor) [18, 19].

In all the cases given in Table I we find two resonances only, one having four times the intensity of the other. We assign these to the *cis* and *trans* cyano resonances respectively. In all cases this pattern is unaffected by addition of free cyanide to the aqueous solutions, indicating that no exchange is occurring. Although a very complex ^{13}C pattern was reported for $[Re(NO)(CN)_5]^{3-}$ and the results attributed to hydrogen bonding effects [17] we find that the spectrum of $[Re(NO)(CN)_5]^{3-}$ is quite normal, exhibiting a δ(*cis*) resonance at 146.7 and δ(*trans*) at 143.6 ppm.

It should be noted that in all our NMR experiments addition of 6 mM $[Gd(EDTA)]^-$ as a relaxation reagent enabled us to accumulate spectral data more rapidly, though chemical shifts were not changed by addition of the reagent. Care has to be taken using this reagent where small splittings of lines are expected since line broadening could render such splittings unobservable.

(c) General Discussion of Results

We attempt here to rationalize the relative values of *k*(*cis*), *k*(*trans*), δ(*cis*) and δ(*trans*). In general we would expect *k*(*cis*) > *k*(*trans*), as found, because the *cis* cyano ligands can form π-bonds with all three t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) while the *trans* ligand has access to only two (d_{xz} and d_{yz}, assuming X to lie on the *z* axis); morevoer it has to compete directly for these latter orbitals with the π-acceptor orbitals of X. The factors causing ^{13}C shifts are complex; paramagnetic shielding effects as well as σ and π bonding contributions play their parts [16, 20, 21] and in cyano complexes anisotropic shielding effects are also important [18]. In general we find that δ(*cis*) > δ(*trans*) (*i.e.*, δ(*trans*) is downfield of δ(*cis*)), suggesting that the *trans* ligand is deshielded relative to the *cis*. That force constants (*k*(*cis*) and *k*(*trans*)) and chemical shifts (δ(*cis*) and δ(*trans*)) follow similar trends is clear from Table I: as *k*(CN) increases for a series of complexes, δ(CN) decreases, a high field shift for the carbon atom indicating that this is more shielded. Similar effects have been noted for pentacarbonyls [16].

(i) Effect of metal oxidation state

Table I shows that, in general, the higher the formal oxidation state of the metal the higher are *k*(*cis*) and *k*(*trans*) (*ca.* 18.4 for Pt^{IV}, 17.5 for Rh^{III}, 16.2 for Fe^{II}). This is to be expected since the higher the metal oxidation state the lower will be the degree of M–C π-bonding leading to a stronger (*i.e.*, higher bond-order) CN bond, with consequent higher ν(CN) and *k*(CN) values. Similarly ^{13}C shifts are lower for high oxidation states – typically δ 85 for Pt^{IV}, 140 for Ru^{IV} and Rh^{III}, 180 for Fe^{II}; these downfield shifts, indicating deshielding of the carbon, are consistent with weaker π-bonding and greater σ-bonding.

(ii) Nature of the ligand and of the metal

Ligand effects are most clearly shown by the two sets of halopentacyano complexes $[MX(CN)_5]^{n-}$ (M = Pt^{IV}, Rh^{III}; X = Cl, Br, I) and by the iron(II) complexes $[FeX(CN)_5]^{n-}$. For the halocomplexes *k*(*cis*) and *k*(*trans*) decrease from X = Cl^- to X = I^-. This probably occurs because in the chloro complexes the metal is effectively more electronegative than in the iodo complex, thus increasing the CN^- to M σ component and decreasing the π component, leading to higher ν(CN) and *k*(CN). Similarly δ(*cis*) and δ(*trans*) decrease slightly from X = Cl to X = I; for X = Cl the CN ligands are relatively shielded but become less so for X = I. Analogous effects were found with $W(CO)_5X$ [16]. For the iron complexes we find that *k*(*cis*) and *k*(*trans*) fall in the sequence $NO^+ \gg CO > NO_2^- > CN^- \sim PPh_3 \sim AsPh_3 > NH_3$, while δ values increase in the same sequence. The above series is approximately that of decreasing π acidity of X (a high π acceptor power for X decreases M–CN π-bonding, thereby increasing ν(CN) and *k*(CN) and decreasing δ(CN), as with pentacarbonyls [16]). A more limited ^{13}C study on $[Fe^{II}L(CN)_5]^{n-}$ showed the same effect on δ for $NO^+ >$ pyrazine $\sim$ CO > pyridine [18, 19], while Mössbauer data on $[Fe^{II}L(CN)_5]^{n-}$ have been interpreted as showing decreasing Fe–L π-bonding for L = $NO^+ > CO > CN^- > PPh_3 > SO_3^{2-} > NO_2^- \sim AsPh_3$ [22], in general agreement with our work.

We have very few data with which to compare *k* and δ values for vertical triads; for *k*(CN) in

$[MH(CN)_5]^{3-}$, Co < Rh < Ir, a sequence also found by Jones for the corresponding hexacyano complexes [23].

(iii) Hydrido and nitrosylpentacyano complexes

We have already noted that in general $k(cis) > k(trans)$ and $\delta(cis) > \delta(trans)$. There are exceptions however; for $[CoH(CN)_5]^{3-}$ and $[Fe(NO)(CN)_5]^{2-}$ $k(trans)$ exceeds $k(cis)$ by almost 0.1, and for $[MH(CN)_5]^{3-}$ (M = Rh, Ir) $\delta(trans) > \delta(cis)$. In the absence of X-ray data for $[CoH(CN)_5]^{3-}$ and also ^{13}C data (unobtainable due to the presence of paramagnetic impurities) the reason for the anomaly is not clear but could arise from kinematic effects – cobalt (and iron) are relatively light, and the Cotton–Kraihanzel assumption that ν(CN) is much higher than any other vibrations is clearly not appropriate for these species (ν(MH) ~ 2100, ν(NO) ~ 1900 cm^{-1}). Coupling of H and CN modes has been clearly demonstrated in $PtH(CN)(PEt_3)_2((CN)_2C_2(CN)_2)$ [24]. In $[Fe(NO)(CN)_5][Fe\,bipy_3]$ an X-ray study shows the *trans* carbon atom to be 0.016 Å closer to the metal than the *cis* carbon atoms, with the metal displaced towards the nitrosyl group (N–Fe–*cis* C 95.0°) [25]; the very strong π-acceptor effect of NO^+ [19] may increase σ-donation from the *trans* cyanide, strengthening the bond and drawing it in.

In $K_3[RhH(CN)_5]$ our X-ray data [1, 14] show the *trans* carbon atom to be 0.08 Å further from the metal than the *cis*, with the rhodium atom displaced towards the *trans* cyanide (H–Rh–*cis* C 87.5°). This distortion (and kinematic effects) may account for $\delta(trans)$ lying higher than $\delta(cis)$ for it and its iridium analogue; furthermore the strong and directional σ-donor and non π-acceptor properties of H^- could well weaken the *trans* CN bond relative to the *cis* and thus bring about deshielding.

(d) X-ray Crystal Structure, Vibrational Spectra and ^{13}C NMR of $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$

The complex was first obtained by us in 1973 [8] and is unusual in being one of the very few nitrido complexes in which the axial and equatorial ligands are the same (another is $[Ru_2N\,en_5]Cl_5$, for which we have published structural, Raman and ^{13}C NMR data [26]). We decided to obtain its X-ray crystal structure since it is the only known binuclear cyano μ-nitrido complex and one of the very few cyano species with a strong π-donor ligand; it may be regarded as a pentacyano complex with a shared central nitrido ligand.

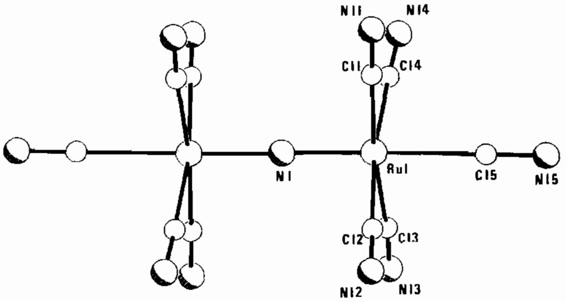

Fig. 1. View of the $[Ru_2N(CN)_{10}]^{5-}$ anion showing the eclipsed conformation of the $Ru(CN)_4$ moieties.

TABLE II. Fractional Atomic Coordinates in $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$, with Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*
Ru(1)	0.11813(10)	0.01199(10)	0.19351(9)
N(1)	0	0	0
C(11)	0.3686(17)	0.2118(17)	0.2400(15)
C(12)	0.0658(17)	0.1999(15)	0.3202(13)
C(13)	−0.1177(16)	−0.1927(15)	0.1649(12)
C(14)	0.1851(16)	−0.1745(14)	0.0943(12)
C(15)	0.2559(16)	0.0258(13)	0.4296(15)
N(11)	0.5103(17)	0.3171(14)	0.2641(14)
N(12)	0.0313(19)	0.2950(13)	0.3856(14)
N(13)	−0.2518(16)	−0.3046(13)	0.1410(13)
N(14)	0.2316(14)	−0.2691(12)	0.0464(12)
N(15)	0.3294(16)	0.0331(17)	0.5550(14)
K(1)	0.4285(4)	0.5876(5)	0.1995(4)
K(2)	0.8892(5)	0.5043(5)	0.2860(4)
K(3)[a]	0.6106(9)	−0.0023(10)	0.1244(9)
O(1)	0.7335(13)	0.3436(12)	0.6012(12)
O(2)[a]	0.3562(23)	−0.0626(22)	−0.1672(21)

[a]These atoms are disordered and have a site occupancy of 0.5.

TABLE III. Bond Lengths (Å) in the $[Ru_2N(CN)_{10}]^{5-}$ Anion with Estimated Standard Deviations in Parentheses

Ru(1)–C(11)	2.059(13)	Ru(1)–C(12)	2.077(15)
Ru(1)–C(13)	2.062(12)	Ru(1)–C(14)	2.068(14)
Mean Ru–C (*cis* to N)	2.067		
Ru(1)–C(15)	2.145(14)	Ru(1)–N(1)	1.766(1)
C(11)–N(11)	1.145(18)	C(12)–N(12)	1.106(22)
C(13)–N(13)	1.125(16)	C(14)–N(14)	1.124(20)
C(15)–N(15)	1.139(20)		

The structure (Fig. 1, Tables II, III and IV) show the anion to be centrosymmetric and have overall idealised D_{4h} symmetry with an eclipsed alignment of the eight *cis* cyano ligands (mean Ru–*cis* C 2.067(14), Ru–*trans* C 2.145(14) Å). The nitrido ligand forms a symmetric linear bridge between the two Ru atoms (Ru–N 1.766(1) Å, compared with 1.742(1) Å for $[Ru_2N\,en_5]Cl_5$ [26] and 1.720(4) Å for $K_3[Ru_2NCl_8(H_2O)_2]$ [27]); as in the latter two complexes the *cis* ligands are bent back from the bridging nitride ligand (mean N–Ru–*cis* C angle 93.1(4)°).

TABLE IV. Bond Angles (°) in the $[Ru_2N(CN)_{10}]^{5-}$ Anion with Estimated Standard Deviations in Parentheses

Ru(1)–N(1)–Ru(1)	180 (by symmetry)		
N(1)–Ru(1)–C(11)	92.9(4)	C(15)–Ru(1)–C(11)	88.2(5)
N(1)–Ru(1)–C(12)	92.8(4)	C(15)–Ru(1)–C(12)	86.3(5)
N(1)–Ru(1)–C(13)	92.6(3)	C(15)–Ru(1)–C(13)	86.4(5)
N(1)–Ru(1)–C(14)	94.0(3)	C(15)–Ru(1)–C(14)	86.9(5)
C(11)–Ru(1)–C(12)	90.4(5)	C(13)–Ru(1)–C(14)	88.2(6)
C(12)–Ru(1)–C(13)	91.2(5)	C(14)–Ru(1)–C(11)	89.6(5)
C(11)–Ru(1)–C(13)	174.2(5)	C(12)–Ru(1)–C(14)	173.2(5)
N(1)–Ru(1)–C(15)	178.6(4)		
Ru(1)–C(11)–N(11)	176.8(1.5)	Ru(1)–C(12)–N(12)	177.3(1.1)
Ru(1)–C(13)–N(13)	176.1(1.2)	Ru(1)–C(14)–N(14)	176.2(9)
Ru(1)–C(15)–N(15)	180.0(1.6)		

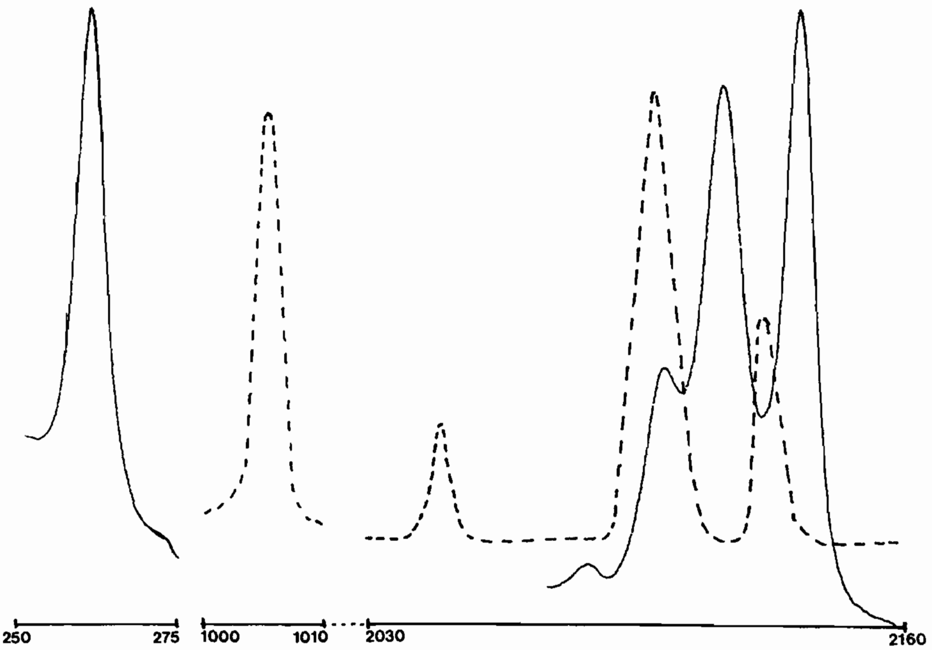

Fig. 2. Raman (solid line) and infrared (dotted line) spectra of aqueous solutions of $K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$. Wavenumbers in cm^{-1}.

The vibrational spectra of the aqueous solution are shown in Fig. 2; we have earlier listed the wavenumbers [8]. The profiles are similar for the solid state and solution suggesting no change of symmetry in solution. In all seven ν(CN) bands, four Raman (two polarised) and three infrared bands, are observed for the aqueous solution, with no coincidences. This unfortunately does not allow us to distinguish between the centrosymmetric D_{4h} (Raman $2A_{1g} + B_{1g} + E_g$, infrared $2A_{2u} + E_u$) and staggered non-centrosymmetric D_{4d} forms (Raman $2A_1 + E_2 + E_3$, infrared $2B_2 + E_1$). The asymmetric $\nu^{as}(Ru_2N)$ stretch is found at 1006 cm^{-1} in aqueous solution and the polarised symmetric $\nu^{s}(Ru_2N)$ at 259 cm^{-1}, close to values found in other μ-nitrido complexes [28].

The data for $[Ru_2N(CN)_{10}]^{5-}$ in Table I show that, if we regard it as a quasi-pentacyano species, $k(cis) > k(trans)$ and $\delta(cis) > \delta(trans)$ as is the case for most pentacyano complexes. It is interesting to note that the chemical shifts for this formally ruthenium(IV) complex are much closer to those for trivalent (e.g., $[Rh(CN)_5X]^{3-}$) than for tetravalent species (e.g., $[Pt(CN)_5X]^{2-}$; $X = Cl^-, Br^-, I^-$). This accords well with our observation that the formally ruthenium(IV) atom in the Ru_2N^{5+} core will associate with ligands which normally stabilise ruthenium(III) or (II) (e.g., en [26], CN^- (this work), bipy, $S_2CNMe_2^-$ [8] and other π-acceptor ligands [29]. Recent ^{99}Ru Mössbauer data on $[Ru_2NX_8(H_2O)_2]^{3-}$ and $[Ru_2N(CN)_{10}]^{5-}$ show low isomer shift values for the halo species and a high isomer shift for the cyanide; this was attributed to metal to cyano π-bonding [30].

(e) Miscellaneous Data: ^{14}N NMR

We have suggested on the basis of analytical, magnetic susceptibility, Raman, resonance Raman and infrared spectroscopy that the reaction product of 'Claus' salt' shown by us to be $Os_3N_2(NH_3)_4(OH)_8(H_2O)_2$ with excess KCN gives $K_4[Os_3N_2(CN)_8(OH)_4(H_2O)_2]$ for which it was proposed that the cyano groups were in equivalent equatorial positions on the end osmium atoms [31]. We observe just one ^{13}C resonance, at δ 145.5 ppm, consistent with this formulation. Reaction of 'osmium violet' ($[Os_3N_2(NH_3)_8(H_2O)_6]Cl_6$) with KCN gives $K_4[Os_3N_2(CN)_{10}(H_2O)_4]$, for which it was suggested that the cyano groups were coordinated to the end metal atoms [31]. The ^{13}C NMR spectra of an aqueous solution of the complex show resonances at δ 147.0 and 143.3 ppm in a 4:1 ratio, presumably due to δ(*cis*) and δ(*trans*) respectively, and in agreement with the proposed structure.

Addition of OsO_4 to excess cyanide give an orange solution for which δ = 115.4 ppm; this is likely to arise from the known *trans*-$[OsO_2(CN)_4]^{2-}$ for which $\nu(CN)$ is at 2152 cm^{-1} [32]. The chemical shift is at a much higher field than that (δ 142.5) reported for $[Os(CN)_6]^{4-}$ [4], consistent with the higher oxidation state in the 'osmyl' complex. Likewise, $[OsO_3N]^-$ reacts with excess cyanide to give a red solution giving only one ^{13}C resonance at δ 118.0 ppm, close to that for *trans*-$[OsO_2(CN)_4]^{2-}$. It is likely to arise from the *trans*-$[OsN(H_2O)(CN)_4]^-$ ion made by reaction of $[OsO_3N]^-$ with liquid HCN [33].

We have measured ^{14}N NMR shifts for two pentacyano complexes (we have previously reported ^{15}N shifts for $[RhH(CN)_5]^{3-}$) [1]. The ^{14}N spectra of $[M(CN)_2]^-$ (M = Cu, Ag); $[Ni(CN)_4]^{2-}$; $[M(CN)_6]^{3-}$ (M = Mn, Fe, Co); $[Fe(CN)_6]^{4-}$ [5] $[Fe(NO)(CN)_5]^{2-}$ and $[Co(NO)(CN)_5]^{3-}$ [34] have been reported; for the nitrosyl complexes no separate ^{14}N resonance for the nitrosyl ligand was seen [34]. We have measured the ^{14}N spectra of CN^- (δ 280.0), $[Pd(CN)_4]^{2-}$ (δ 266), $[Pt(CN)_4]^{2-}$ (δ 280), $[Mo(CN)_8]^{4-}$ (δ 355) and $[W(CN)_8]^{4-}$ (δ 290), $[RhH(CN)_5]^{3-}$ (δ 259) and $[PtCl(CN)_5]^{2-}$ (δ 300) (all relative to NH_4^+ in NH_4NO_3 = 0). There is no substantial broadening for the pentacyano *versus* the hexacyano species; we cannot, however, from our data and those of refs. 5 and 34 detect any patterns in the shifts for the different complexes, e.g., with coordination number or oxidation state. This is perhaps because the nitrogen atom is well removed from the vicinity of the metal. In no cases could we observe separate resonances for *cis* and *trans* cyano groups – perhaps because of the breadth of the lines – and no metal-^{14}N coupling was observed. We conclude that ^{14}N NMR is not useful for our purposes with pentacyano complexes: ^{15}N NMR, though in practice more difficult to obtain, should be useful since sharper lines and couplings would be expected.

Experimental

Complexes are dealt with in the order of Table I.

$K_3[CoH(CN)_5]$. This was prepared *in situ* as in the literature [35].

$K_3[RhH(CN)_5]$ and $K_3[IrH(CN)_5]$. These were made as described in ref. 14.

$[RhX(CN)_5]^{3-}$ (X = Cl, Br, I). These were made *in situ* as in the literature and not isolated [36].

$Na_3[Fe(CO)(CN)_5]$. A solution of $Na_3[Fe(NH_3)(CN)_5]$ prepared as below was treated with carbon monoxide gas until the colour changed from yellow to colourless [37]. This solution was used for all measurements.

$Na_3[Fe(PPh_3)(CN)_5]\cdot 2H_2O$. Prepared as in ref. 38. *Anal.* Found: C, 49.5; H, 3.4; N, 12.3. Calc. for $C_{23}FeH_{19}Na_3O_2P$: C, 49.9; H, 3.4; N, 12.7%.

$Na_3[Fe(AsPh_3)(CN)_5]\cdot 2H_2O$. Prepared by a method analogous to that in ref. 38. *Anal.* Found: C, 45.2; H, 3.2; N, 11.8. Calc. for $AsC_{23}FeH_{19}Na_3O_2$: C, 46.2; H, 3.2; N, 11.7%.

$Na_3[Fe(pyridine)(CN)_5]$ [39] and $Na_5[Fe(SO)_3)(CN)_5]$ [40]. Prepared by literature methods.

$Na_3[Fe(NH_3)(CN)_5]\cdot 3H_2O$. This was prepared as in ref. 37. *Anal.* Found: C, 18.3; H, 2.8; N, 25.5. Calc. for $C_5FeH_9N_6Na_3O_3$: C, 18.4; H, 2.8; N, 25.8%.

$K_5[Ru_2N(CN)_{10}]\cdot 3H_2O$. Prepared as in ref. 8. *Anal.* Found: C, 16.4; H, 0.8; K, 26.8; N, 21.2. Calc. for $C_{10}H_6K_5N_{11}O_3Ru_2$: C, 16.6; H, 0.8; H, 26.9; N, 21.2%.

$[PtX(CN)_5]^{2-}$ (X = Cl, Br, I). The complexes were prepared in solution as in ref. 41 and not isolated.

$K_3[Re(NO)(CN)_5]\cdot 2H_2O$. The complex was prepared using the method described for $K_3[Re(NO)(CN)_7]\cdot 4H_2O$ [42]. *Anal.* Found: C, 11.8; H, 0.8; N, 16.75. Calc. for $C_5H_4K_3N_6O_3Re$: C, 12.0; H, 0.8; N, 16.8%.

$K_4[Os_3N_2(CN)_8(OH)_4(OH_2)_2]$ [31]. The complex $Os_3N_2(NH_3)_4(OH)_8(OH_2)_2$ (1.0 g, 1.2 mmol)

was dissolved in potassium cyanide solution (2.5 g in 75 cm^3 water) and the mixture heated under reflux for 7 h. When cold, the brown solution was added to methanol (150 cm^3) and the brown product filtered off and washed with methanol and ether. *Anal.* Found: C, 8.9; H, 1.0; N, 13.7. Calc. For $C_8H_8K_4N_{10}O_6Os_3$: C, 9.0; H, 0.8; N, 13.1%.

$K_4[Os_3N_2(CN)_{10}(OH_2)_4]\cdot 4H_2O$ [31]. The complex $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$ (0.35 g, 0.33 mmol) was dissolved in potassium cyanide solution (2.0 g in 5 cm^3 water) and the mixture stirred and heated under reflux for 7 h. The brown solution was added to methanol (20 cm^3), the product filtered, washed with methanol and ether and recrystallised from water/methanol. *Anal.* Found: C, 9.8; H, 1.4; N, 14.6. Calc. for $C_{10}H_{16}K_4N_{12}O_8Os_3$: C, 10.4; H, 1.4; N, 14.5%.

Raman spectra were measured on a Spex Ramalog 5 spectrometer with a CRL-52 krypton ion laser at 6471 and 5682 Å on spinning discs on KBr (solid) or in spinning solution cells; infrared spectra were measured on a Perkin-Elmer 683 instrument with liquid paraffin mulls between CsI plates (solids) or as aqueous solutions between CaF_2 plates.

^{13}C spectra were measured on a Jeol FX90Q instrument and ^{14}N NMR spectra at 6.43 mHz on the same instrument. For the ^{14}N spectra we find that the best results were obtained at pulse delays of one second and pulse widths of 30 μs; typically 500 to 1000 scans were required for good results. A 2 M NH_4NO_3 solution was used as a standard, for which $\delta(NH_4) = 0$ and $\delta(NO_3^-) = 355.8$ ppm. Microanalyses were performed by the Microanalytical Department, Imperial College.

Crystallographic Studies

Measurements were carried out on a Nicolet R3m/Eclipse S140 diffractometer system with graphite-monochromated Cu Kα radiation. The crystal selected for intensity data collection was irregular in shape and of approximate dimensions 0.16 × 0.14 × 0.09 mm. Unit-cell dimensions were determined by least-squares refinement of the angular settings of 18 automatically centred reflections.

Crystal Data.

Formula $C_{10}H_6K_5N_{11}O_3Ru_2$, $M = 725.9$, triclinic, $a = 8.757(2)$, $b = 9.121(3)$, $c = 9.444(2)$ Å, $\alpha = 106.81(2)$, $\beta = 106.91(2)$, $\gamma = 112.52(2)^\circ$, $U = 594.3$ Å^3 (at 19 °C), space group $P\bar{1}$, $Z = 1$, $D_c = 2.03$ g cm^{-3}, $F(000) = 344.9$, $\mu(\text{Cu K}\alpha) = 189.2$ cm^{-1}.

Integrated intensities in one hemisphere were measured using the ω-scan technique. Two reflections (21$\bar{1}$ and 002) were monitored every 50 measurements, and showed no significant variation in their intensities. A total of 1496 independent reflections were measured (to $\theta = 55^\circ$), of which 71 were judged to be 'unobserved' ($F < 3\sigma(F)$). The data were scaled using the reference reflections and were corrected for Lorentz and polarisation effects. In the later stages of refinement an empirical absorption correction was applied [43] based on 36 psi-scan measurements from each of 9 representative reflections.

All calculations and drawings were made using the SHELXTL program system [43], and the atomic scattering factors and anomalous dispersion corrections were taken from ref. 44.

The coordinates of the ruthenium atom were derived from an initial Patterson synthesis, and the positions of all other non-hydrogen atoms were found from subsequent difference Fourier syntheses. Least-squares refinement was by the block cascade method typical of the SHELXTL system. All atoms were refined with anisotropic temperature parameters, and two atoms showing positional disorder were given site occupancy factors of 0.5. A weighting scheme was applied so that $w = 1/[\sigma(F_o)^2 + 0.00065F_o^2]$ for the last cycle, and the final value of R was 0.064.

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