Molecular Structure and Linkage Isomerism of *cis*-[Ru(bipy)$_2$-{*trans*-Cr(cyclam)(CN)$_2$}$_2$]$^{4+}$ (bipy = 2,2′-bipyridine, cyclam = 1,4,8,11-tetraazacyclotetradecane)†

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The molecular structure of the trinuclear complex *cis*-[Ru(bipy)$_2${*trans*-Cr(cyclam)(CN)$_2$}$_2$]$^{4+}$ (bipy = 2,2′-bipyridine, cyclam = 1,4,8,11-tetraazacyclotetradecane) has been determined by X-ray diffraction. The co-ordination octahedra of the ruthenium(II) and chromium(III) units are staggered, and a modest deviation from linearity is observed in the Ru–(NC)–Cr units. The binding mode of the bridging cyanides, not obtainable from the crystallographic data, was demonstrated to be –Ru^{II}–NC–Cr^{III}– by infrared spectroscopy. This binding mode is imposed by synthesis, but is not the thermodynamically stable one. Indeed, linkage isomerization of the bridging ligands can be induced by heating the complex in the solid state (several hours at 150 °C). The flip of the bridging cyanide is clearly detectable by infrared spectroscopy. The photophysical properties of the –Ru^{II}–CN–Cr^{III}– linkage isomer, featuring efficient transfer of excitation energy from the Ru(bipy)$_2{}^{2+}$ chromophore to the emitting chromium(III) fragment, have been studied.

Considerable interest has been devoted in the last few years to the photophysics of supramolecular systems.[1] The study of such systems is seen as a step towards the development of photochemical molecular devices, *i.e.* artificial systems capable of performing useful light-induced functions.[1,2] In this context, several covalently linked supermolecules made up of both organic[1,3–5] and inorganic[1,6,7] molecular components have been synthesised and studied. A particularly interesting class of inorganic supermolecules is that schematized as M(NC)Ru(bipy)$_2$(CN)M, in which the *cis*-Ru(bipy)$_2{}^{2+}$ chromophore (bipy = 2,2′-bipyridine) is linked *via* cyanide bridges to various metal-containing fragments M.[1,7–18] The bridging cyanides promote a relatively strong electronic coupling between the metal units, though still allowing an essentially valence-localized description of the polynuclear complexes. Depending on the nature of the M components, perturbation of the properties of the Ru⟶bipy metal-to-ligand charge-transfer (m.l.c.t.) excited state,[9,10] intercomponent electron-transfer quenching,[7,11–13] or intercomponent exchange energy-transfer processes[7,8,13–18] have been observed in this class of compounds.

Systems of the above type with chromium(III) complex fragments as M are particularly suited for the study of intercomponent energy-transfer processes, because of the characteristic luminophoric properties of these units.[7,8,15,18] In an attempt to achieve optimum properties within this class of compounds (efficient chromophore ⟶ luminophore energy transfer, high chemical and photochemical stability, solvent-independent emission behaviour, high emission quantum yields), we have recently synthesised the trinuclear complex *cis*-[Ru(bipy)$_2${*trans*-Cr(cyclam)(CN)$_2$}$_2$]$^{4+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane). A detailed account of the photophysical properties has been given elsewhere.[18] We report here the molecular structure of this complex. This is the first case within this family of compounds, and one of the few cases among trinuclear complexes in general, for which direct structural information is available from X-ray crystallography. The binding mode of the bridging cyanide in this complex (–Ru–NC–Cr–), a feature which is not obtainable from the crystal structure on pure refinement grounds, has been inferred from infrared spectroscopic data. The spectroscopic study has led to the discovery of a thermally activated solid-state linkage isomerization reaction. The photophysical properties of the linkage isomer (–Ru–CN–Cr–) are also reported.

Experimental

Materials.—The complexes *trans*-[Cr(cyclam)(CN)$_2$]Cl,[19] *cis*-[Ru(bipy)$_2$(CN)$_2$][20] and *cis*-[Ru(bipy)$_2${*trans*-Cr(cyclam)(CN)$_2$}$_2$][PF$_6$]$_3$Cl·2H$_2$O[18] were prepared following previously reported procedures. Crystals suitable for X-ray structural determination were obtained by slow crystallization of *cis*-[Ru(bipy)$_2${*trans*-Cr(cyclam)(CN)$_2$}$_2$][PF$_6$]$_3$Cl·2H$_2$O from MeCN–MeOH (1 : 1) solution.

Apparatus and Procedures.—The UV/VIS absorption, emission and lifetime measurements were performed with previously described apparatus.[18] Emission quantum yields were obtained, at room temperature in water solutions, from corrected emission spectra relative to [Ru(bipy)$_3$]$^{2+}$ (Φ = 0.042).[21] Infrared spectra were recorded on KBr pellets with an IFS88 Bruker FTIR spectrophotometer.

X-Ray Analysis.—X-Ray data collected from the best crystal, obtained after many recrystallizations, showed that the crystallinity of the sample was rather poor. Attempts to improve the quality of the crystals by substituting the PF$_6{}^-$ and Cl$^-$ with different anions including tetraphenylborate, toluene-*p*-sulfonate, benzene-1,4-disulfonate and sulfate were unsuccessful.

Crystal data. C$_{44}$H$_{68}$ClCr$_2$F$_{18}$N$_{16}$O$_2$P$_3$Ru, M = 1528.5, monoclinic, space group $I2/a$ (alternative $C2/c$, no. 15), a = 31.528(5), b = 12.578(2), c = 36.411(3) Å, β = 112.27(2)°,

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

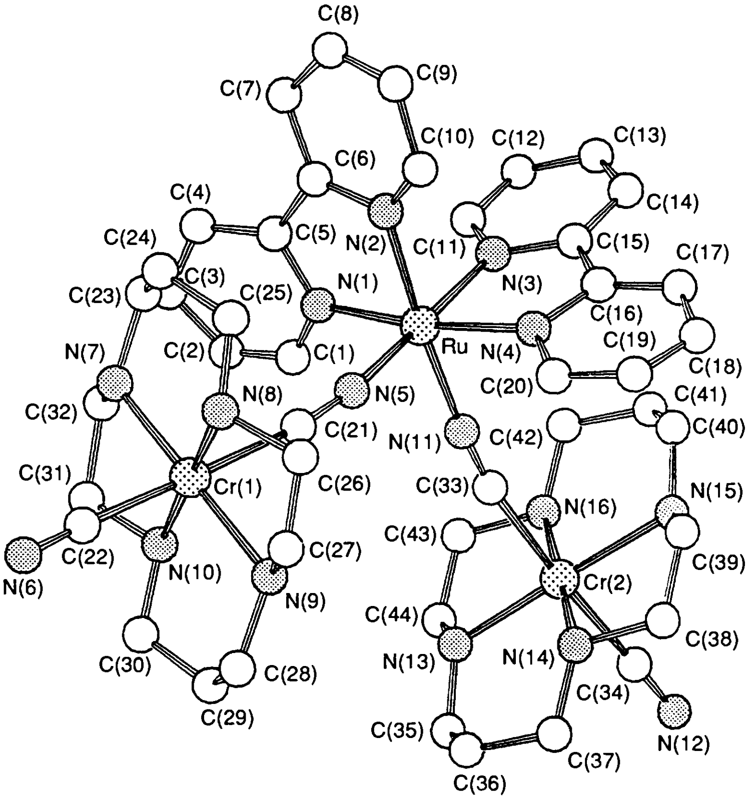

Fig. 1 Molecular structure of the trinuclear complex ion *cis*-$[Ru(bipy)_2\{trans\text{-}Cr(cyclam)(CN)_2\}_2]^{4+}$

$U = 13\,362(4)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range $8 \leqslant \theta \leqslant 11°$, $\lambda = 0.710\,69$ Å), $Z = 8$, $D_c = 1.52$ g cm^{-3}, $F(000) = 6208$. Red-orange crystals of dimensions 0.19 × 0.24 × 0.38 mm, μ(Mo-Kα) = 7.36 cm^{-1}.

Data collection and processing. CAD4 Diffractometer, ω–2θ scan mode, graphite-monochromated Mo-Kα radiation; 8213 unique reflections measured ($2 \leqslant \theta \leqslant 21°$, $+h, +k, \pm l$) of which 2627 were considered observed [$I \geqslant 3\sigma(I)$]. The data were corrected for Lorentz, polarization and absorption effects (ψ-scan method, minimum transmission factor = 0.94).

Structure analysis and refinement. Solution by direct methods followed by normal Fourier procedures. Full-matrix least-squares refinement (in three blocks for the final cycles). The Ru, Cr, Cl and N atoms were refined anisotropically, other non-hydrogen atoms isotropically. The hydrogen atoms were included in idealized positions. The weighting scheme $w = 4F_o/[\sigma^2(F_o) + 0.08(F_o)^2]^2$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analysis. Final R and R' 0.100 and 0.120. Programs and sources of scattering factors are given in ref. 22.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

The data were collected in the limited range of $2 \leqslant \theta \leqslant 21°$, however they turned out to be sufficient to allow an unequivocal determination of the overall structure. The crystal displayed a certain degree of disorder; however, the trinuclear cation was the best determined part of the structure because the disorder was localized in the PF_6^- anions and water molecules. The three PF_6^- anions display different types of disorder. Two are disordered over two positions and the atoms were refined isotropically with occupancy 0.5. Owing to instability during the refinement some F atoms were refined using fixed thermal parameters. The third PF_6^- anion was found from very low peaks on the final ΔF map and was refined using fixed and very high thermal parameters for all the atoms. A Cl^- ion and a water molecule O(1w) were found in general position, while two other water molecules were found in special positions, in particular O(2w) on a two-fold axis and O(3w) disordered around another two-fold axis. The hexafluorophosphate anions are not involved in short contacts, while the Cl^- anion and water molecules form a network of hydrogen bonds with distances Cl···O(1w) 3.14(3), Cl···O(2w) 3.09(2) and O(1w)···O(3w) 2.98(10) Å. Refinement was carried out anisotropically only for Ru, Cr, Cl and N atoms and final estimated standard deviations (e.s.d.s) are in the range 0.02–0.03 Å on metal–nitrogen/carbon and 0.03–0.05 Å on carbon–carbon distances. The C and N atoms of the CN bridges are indistinguishable on pure refinement grounds and it has been assumed that carbon is connected to Cr^{III} and nitrogen to Ru^{II} in view of the method of preparation {starting from $[Cr(cyclam)(CN)_2]^+$ and $[Ru(bipy)_2Cl_2]$[18]} and from FTIR spectra (see Discussion). The cationic complex was characterized as *cis*-$[Ru(bipy)_2\{trans\text{-}Cr(cyclam)(CN)_2\}_2]^{4+}$ (Fig. 1) and the crystal as an association of the trinuclear complex, PF_6^- and Cl^- anions, and water molecules in the ratio 1:3:1:2, respectively. Atomic coordinates for the cation complex are given in Table 1, and selected bond distances and angles in Table 2.

Thermal Effects on Spectroscopic and Photophysical Properties.—The FTIR spectra were recorded in the 4000–400 cm^{-1} spectral region. In the 2000–400 cm^{-1} range the spectrum of *cis*-$[Ru(bipy)_2\{trans\text{-}Cr(cyclam)(CN)_2\}_2][PF_6]_3Cl\cdot 2H_2O$ was observed to be an almost exact superposition of the spectra of *trans*-$[Cr(cyclam)(CN)_2]Cl$ and *cis*-$[Ru(bipy)_2(CN)_2]$. Cyanide stretching bands, ν(CN), were observed at 2133m and 2062vw cm^{-1}. Heating the complex in the solid state, either as a pure powder or in KBr pellets, was observed to cause (besides the disappearance of bands due to water of crystallization at

Table 1 Positional parameters (× 10⁴) with e.s.d.s in parentheses for *cis*-[Ru(bipy)$_2${*trans*-Cr(cyclam)(CN)$_2$}$_2$]$^{4+}$

Atom	*x*	*y*	*z*
Ru	4015.9(7)	4066(2)	1207.5(5)
N(1)	4718(6)	3922(16)	1462(5)
N(2)	4212(6)	4962(16)	832(5)
N(3)	3991(7)	5496(17)	1487(6)
N(4)	3333(7)	4435(18)	947(5)
C(1)	4960(8)	3286(22)	1765(7)
C(2)	5404(12)	3109(30)	1894(10)
C(3)	5654(10)	3683(25)	1698(9)
C(4)	5412(10)	4282(25)	1387(8)
C(5)	4959(9)	4471(22)	1267(8)
C(6)	4658(8)	5055(21)	920(7)
C(7)	4830(11)	5738(28)	681(9)
C(8)	4521(11)	6191(28)	404(10)
C(9)	4071(12)	6102(32)	239(11)
C(10)	3939(10)	5474(26)	499(9)
C(11)	4351(9)	5963(26)	1763(8)
C(12)	4313(10)	6981(25)	1890(8)
C(13)	3913(10)	7429(27)	1748(9)
C(14)	3500(11)	6980(28)	1455(9)
C(15)	3568(8)	5931(25)	1331(7)
C(16)	3194(9)	5401(23)	1039(8)
C(17)	2768(11)	5680(28)	891(9)
C(18)	2406(13)	5038(32)	626(11)
C(19)	2568(12)	4044(33)	536(10)
C(20)	3031(9)	3812(23)	701(8)
Cr(1)	4234(1)	828(4)	397(1)
N(5)	4038(6)	2743(17)	904(5)
N(6)	4517(8)	−874(22)	−86(7)
N(7)	4875(7)	1592(20)	517(6)
N(8)	3917(6)	1706(19)	−120(5)
N(9)	3629(7)	112(17)	278(5)
N(10)	4550(8)	−52(22)	902(6)
C(21)	4074(7)	2011(21)	725(6)
C(22)	4406(8)	−305(22)	84(8)
C(23)	4883(10)	2643(26)	442(9)
C(24)	4567(9)	2981(24)	46(8)
C(25)	4066(11)	2779(28)	−90(9)
C(26)	3435(12)	1446(30)	−197(10)
C(27)	3356(10)	360(25)	−95(8)
C(28)	3622(10)	−1023(27)	382(8)
C(29)	3973(12)	−1279(29)	788(10)
C(30)	4429(11)	−1078(28)	911(9)
C(31)	5051(11)	178(29)	1010(10)
C(32)	5150(11)	1226(27)	941(9)
Cr(2)	3315(1)	2238(4)	2134(1)
N(11)	3853(6)	3227(16)	1618(5)
N(12)	2784(7)	1320(20)	2657(6)
N(13)	3743(6)	918(18)	2315(5)
N(14)	2867(7)	1499(18)	1623(5)
N(15)	2870(6)	3462(18)	1952(5)
N(16)	3763(6)	2992(18)	2646(6)
C(33)	3661(7)	2798(20)	1798(7)
C(34)	2971(8)	1624(22)	2466(7)
C(35)	3565(9)	−98(24)	2247(7)
C(36)	3208(9)	−348(23)	1845(7)
C(37)	2796(9)	370(24)	1684(8)
C(38)	2443(10)	2152(25)	1472(8)
C(39)	2573(9)	3262(24)	1532(8)
C(40)	3058(9)	4564(22)	2024(7)
C(41)	3383(12)	4698(31)	2446(10)
C(42)	3822(10)	4097(28)	2616(8)
C(43)	4193(9)	2298(24)	2788(8)
C(44)	4060(10)	1181(24)	2746(8)

Table 2 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

Ru–N(1)	2.06(2)	Cr(1)–C(22)	2.03(3)
Ru–N(2)	2.04(2)	Cr(2)–N(13)	2.09(2)
Ru–N(3)	2.08(2)	Cr(2)–N(14)	2.08(2)
Ru–N(4)	2.05(2)	Cr(2)–N(15)	2.02(2)
Ru–N(5)	2.01(2)	Cr(2)–N(16)	2.09(2)
Ru–N(11)	2.05(2)	Cr(2)–C(33)	2.07(3)
Cr(1)–N(7)	2.13(2)	Cr(2)–C(34)	2.05(3)
Cr(1)–N(8)	2.08(2)	N(5)–C(21)	1.16(3)
Cr(1)–N(9)	2.00(2)	N(6)–C(22)	1.09(4)
Cr(1)–N(10)	2.05(2)	N(11)–C(33)	1.15(4)
Cr(1)–C(21)	2.08(3)	N(12)–C(34)	1.14(4)
N(1)–Ru–N(2)	78.7(7)	N(4)–Ru–N(5)	100.4(7)
N(1)–Ru–N(3)	95.2(8)	N(4)–Ru–N(11)	86.8(8)
N(1)–Ru–N(4)	171.9(9)	N(5)–Ru–N(11)	92.6(8)
N(1)–Ru–N(5)	85.4(7)	C(21)–Cr(1)–C(22)	178(1)
N(1)–Ru–N(11)	98.7(7)	C(33)–Cr(2)–C(34)	178(1)
N(2)–Ru–N(3)	85.9(9)	Ru–N(5)–C(21)	176(2)
N(2)–Ru–N(4)	95.5(8)	Ru–N(11)–C(33)	164(2)
N(2)–Ru–N(5)	90.3(8)	Cr(1)–C(21)–N(5)	170(2)
N(2)–Ru–N(11)	175.9(7)	Cr(1)–C(22)–N(6)	176(3)
N(3)–Ru–N(4)	78.7(8)	Cr(2)–C(33)–N(11)	172(2)
N(3)–Ru–N(5)	176.0(8)	Cr(2)–C(34)–N(12)	177(2)
N(3)–Ru–N(11)	91.3(9)		

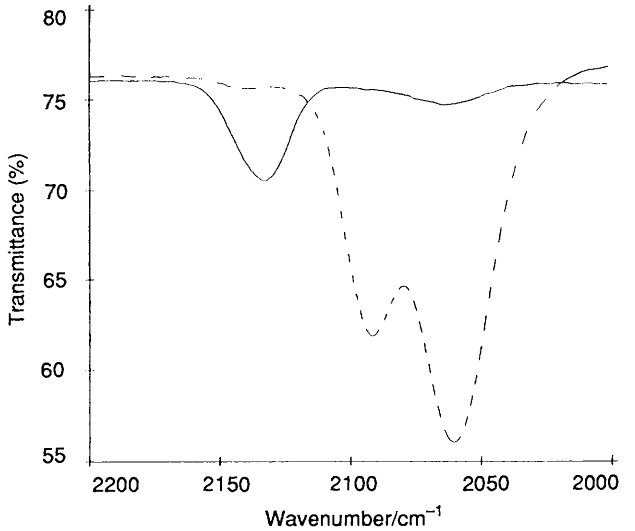

Fig. 2 Infrared spectra (cyanide stretching region) of the trinuclear complex, before (——) and after (– – – –) heating (6 h at 150 °C, KBr pellet)

1634 and 3440 cm^{-1}) a decrease in intensity of ν(CN) at 2133 cm^{-1} and the appearance of two new, strong bands at 2091 and 2060 cm^{-1} (Fig. 2). These spectral changes were complete after 6 h of heating at 150 °C and no appreciable variation in energy and intensity of the other bands in the 4000–400 cm^{-1} region was observed. An analogous behaviour was exhibited by the trinuclear complex K$_4$[*cis*-Ru(bipy)$_2${Cr(CN)$_6$}$_2$].[15] In the cyanide stretching region this species exhibits bands at 2130m cm^{-1} {coinciding with ν(CN) of [Cr(CN)$_6$]$^{3-}$} and 2080w cm^{-1}. Heating in KBr pellets caused the appearance of two new strong bands at 2072 and 2096 cm^{-1}. No further spectral changes were observed after 2 h of heating at 120 °C.

After prolonged heating (6 h) at 150 °C, solid samples of *cis*-[Ru(bipy)$_2${*trans*-Cr(cyclam)(CN)$_2$}$_2$][PF$_6$]$_3$Cl·2H$_2$O were dissolved in aqueous solutions containing 1 × 10^{-3} mol dm^{-3} HClO$_4$ for absorption/emission monitoring. The absorption and emission spectra so obtained are shown in Fig. 3, together with those of the starting complex. The effect of heating is to shift the lowest m.l.c.t. absorption band from 440 (lowest-energy shoulder) to 390 nm, and the emission maximum from 727 to 722 nm. The excitation spectra of both solutions were found to be superimposable on the corresponding visible

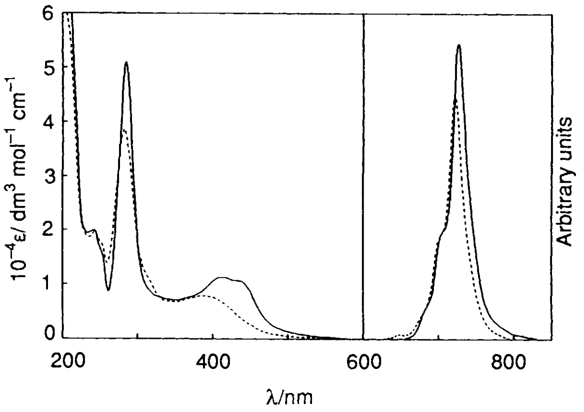

Fig. 3 Absorption and emission spectra of aqueous solutions obtained by dissolving the trinuclear complex before (——) and after (- - - -) heating in the solid state (6 h at 150 °C)

Table 3 Emission properties of the bridge linkage isomers of *cis*-[Ru(bipy)$_2${*trans*-Cr(cyclam)(CN)$_2$}$_2$]$^{4+}$ in aqueous solution *

Isomer	λ_{max}/nm	τ/μs	$10^3\Phi$
–Ru^{II}–NC–Cr^{III}–	727	260	5.3
–Ru^{II}–CN–Cr^{III}–	722	240	4.4

* Degassed solutions containing 1×10^{-3} mol dm^{-3} $HClO_4$.

absorption spectra. The emission lifetimes and quantum yields of solutions of unheated and heated samples are compared in Table 3 (for the identification of the emitting species, see Discussion). No changes in absorption and emission were observed in the dark 2 d after the preparation of solutions of the heated sample. Some photochemical instability {$\Phi \approx 10^{-3}$, formation of free [Ru(bipy)$_2$(CN)$_2$]} was, however, detected upon prolonged visible irradiation of such solutions.

Discussion

Molecular Structure.—The structure of the trinuclear complex (Fig. 1) shows that the co-ordination around the Ru and Cr atoms is approximately octahedral and the complex ion as a whole displays almost perfect C_2 symmetry around an axis passing through the Ru atom and the midpoint between the two chromium centres. Since the C and N atoms cannot be distinguished on pure refinement grounds, the arrangement of the bridging cyanides (C bonded to Cr and N to Ru) depicted is that dictated by the synthetic procedure used,[18] assuming that no linkage isomerization occurred under the reaction conditions used. This arrangement is confirmed by the spectroscopic data and chemical behaviour (see below). Two features can be noticed from Fig. 1: (*i*) the Cr-based octahedra are staggered with respect to the Ru-based octahedron; (*ii*) the Ru-cyanide-Cr bridges are clearly bent [angles at N(5), N(11), C(21) and C(33) 176, 164, 170 and 172°, respectively]. These situations are not common, as shown, *e.g.*, by a sample of five non-polymeric structures having two octahedral metal centres bridged by a cyanide group,[23] where a staggered geometry is only observed once,[23a] while the angles at the bridging atoms do not deviate substantially from linearity. It seems difficult to find explanations for effects (*i*) and (*ii*) based on purely electronic arguments or on steric effects at the molecular level. The other features of the structure are largely as expected. The Cr–N (cyclam) and Cr–C (cyanide) lengths [average 2.07(4) and 2.06(3) Å, respectively] are comparable to the corresponding distances in mononuclear *trans*-[Cr(cyclam)(CN)$_2$]$^+$ [2.065(4) and 2.089(4) Å, respectively].[24] The Ru–N (bipy) distances [average 2.006(2) Å] fall in the range of those in other monomeric Ru(bipy) complexes (2.01–2.11 Å),[25] and the Ru–N (cyanide) distances [average 2.03(2) Å] are similar to that observed for [Ru(bipy)$_2$(MeCN)$_2$]$^{2+}$ complex [2.033(7) Å].[25b] The last observation supports previous spectroscopic arguments suggesting consideration of the NC–Cr(cyclam)–CN$^+$ complex as a pseudo-nitrile 'ligand'.[18]

Linkage Isomerism.—A way to distinguish between the two possible arrangements of the bridging cyanides, –Ru^{II}–NC–Cr^{III}– and –Ru^{II}–CN–Cr^{III}–, is afforded by infrared spectroscopy.[26] In simple mononuclear cyanide complexes both the *frequency* and *intensity* of the cyanide IR stretching bands are very sensitive to the nature and oxidation state of the metal.[26b,c,27] The frequency depends obviously on the degree of bond weakening induced by back donation from the metal. Therefore, lower frequencies are expected for cyanides co-ordinated to electron-rich metals relative to electron-poor ones. On the other hand, band intensities are related to the magnitude of the dipole-moment changes accompanying the C–N stretching vibration. During such a vibration, back donation from the metal is modulated by the energy changes of the π* orbitals of cyanide, producing an oscillating dipole along the metal–ligand coordinate. The magnitude of this effect again depends on the metal. With an electron-rich metal, π-back bonding is more efficient, and more intense IR stretching bands are expected. The IR spectra of [Ru(bipy)$_2$(CN)$_2$] and [Cr(cyclam)(CN)$_2$]$^+$ clearly exemplify the above features. For the ruthenium(II) complex very intense cyanide stretching bands are found at 2053 and 2067 cm^{-1},[27] whereas for the chromium(III) complex these bands are much weaker (by two orders of magnitude) and occur at 2100 and 2138 cm^{-1}. The presence of two CN stretching frequencies probably reflects the presence of both free and hydrated (hydrogen-bonded) cyanides. Samples of [Cr(cyclam)(CN)$_2$]Cl from different crystallizations were found to differ in the relative intensity of the two bands. It seems likely that varying degrees of hydration are at the origin of these observations. In a previous report[19] a band at 2090 cm^{-1} was quoted.

For a bridging cyanide the prediction of such effects is complicated by the presence of two potential sites for back bonding. In practice, however, π metal–ligand bonding seems to be much more important at the carbon-end of a bridging cyanide than at the N. This conclusion is based on the structure of stable mixed-valence or bimetallic cyanides,[28] where cyanide is invariably C-bonded to the more electron-rich metal {*viz.* the –Fe^{II}–CN–Fe^{III}– arrangement of Prussian Blue, KFe[Fe(CN)$_6$]},[29] and is consistent with the infrared spectroscopy of several cyano-bridged polynuclear complexes.[26,27] Thus, the Ru^{II}–NC–Cr^{III} and a Ru^{II}–CN–Cr^{III} binding modes are expected to differ in the cyanide-stretching region of their IR spectra. The bands are expected to be more intense and at lower frequency when cyanide is C-bonded to Ru^{II} than when it is C-bonded to Cr^{III}.

The synthetic route followed to produce the trinuclear complex {reaction between [Cr(cyclam)(CN)$_2$]$^+$ and [Ru(bipy)$_2$Cl$_2$]}[18] implies the –Ru^{II}–NC–Cr^{III}– binding mode, at least as a primary product. Given the already noted general preference of the carbon end of cyanide for the more electron-rich metal, this binding mode is likely to be the 'wrong' one, and a linkage isomerization leading to the stable –Ru^{II}–CN–Cr^{III}– isomer is expected to be thermodynamically allowed.[30] The results show that, although the complex obtained by synthesis is kinetically stable at room temperature, it undergoes reaction in the solid state upon prolonged heating. The fact that the reaction indeed involves a flip of the bridging cyanides from C bonded to Cr^{III} to C bonded to Ru^{II} is demonstrated by the changes in the IR spectrum (Fig. 2), which shows the expected increase in intensity and shift to low frequency. The fact that the solid-state reaction is a clean linkage isomerization [equation (1)], without decomposition of the trinuclear complex, is

$$[\mathrm{NC{-}Cr(cyclam){-}CN{-}Ru(bipy)_2{-}NC{-}Cr(cyclam){-}CN}]^{4+} \longrightarrow [\mathrm{NC{-}Cr(cyclam){-}NC{-}Ru(bipy)_2{-}CN{-}Cr(cyclam){-}CN}]^{4+} \quad (1)$$

demonstrated by the photophysical results obtained for aqueous solutions of the reacted material. The position of the visible m.l.c.t. band (blue shifted with respect to the starting isomer) is consistent with the expected increase in π-back donation from $\mathrm{Ru^{II}}$ upon isomerization, and is as expected on the basis of previous experience with related $\mathrm{M^{III}{-}NC{-}Ru(bipy)_2{-}CN{-}M^{III}}$ complexes [*e.g.* λ_{max} = 385 nm for $\mathrm{M^{III}} = \mathrm{Ru(NH_3)_5{}^{3+}}$].[11] The lack of any Ru-based m.l.c.t. emission, the presence of a typical chromium(III) emission, and the coincidence between excitation and emission spectra indicate that, as already observed for the starting $\mathrm{{-}Ru^{II}{-}NC{-}Cr^{III}{-}}$ linkage isomer,[18] efficient intercomponent energy transfer across the cyanide bridges takes place in the isomerized system as well. The small shift observed in emission is consistent with the fact that the energy of the emitting state (intraconfigurational $t_{2g}{}^3$ doublet) depends only slightly on the ligands, through their nephelauxetic effect.[31] The direction of the shift seems to indicate a slightly smaller nephelauxetic effect at $\mathrm{Cr^{III}}$ of N- relative to C-bonded cyanide.

Conclusion

In the molecular structure of the *cis*-$[\mathrm{Ru(bipy)_2\{}$*trans*-$\mathrm{Cr(cyclam)(CN)_2\}_2}]^{4+}$ trinuclear complex ion, as determined in this work by X-ray diffraction, the binding mode of the bridging cyanides remains undetermined. The study of thermal effects on solid samples of the trinuclear complex using infrared spectroscopy (in the cyanide-stretching region) shows that: (*i*) the trinuclear complex obtained from synthesis has the thermodynamically 'wrong' arrangement, with bridging cyanides C-bonded to $\mathrm{Cr^{III}}$; (*ii*) heating of the complex in the solid state induces a clean bridge linkage-isomerization reaction (cyanide flip). The solid-state isomerization reaction observed in this work is of preparative value, allowing the isolation of the two linkage isomers of a cyano-bridged bimetallic complex. The strategy, *i.e.* synthesis orienting towards the less thermodynamically favoured bridging mode, followed by thermal solid-state isomerization, could be of general use in this class of compounds.

Acknowledgements

This work was supported by the Ministero della Università e Ricerca Scientifica and by the Consiglio Nazionale delle Ricerche (Progetto Finalizzato Chimica Fine).

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Received 16*th March* 1994; *Paper* 4/01573H