# The crystal and molecular structure of sodium hexacyanoosmate(II) decahydrate and related hexacyanometalate complexes

**Luis A. Gentil**
*Departamento de Ingeniería Química, Universidad Nacional de Mar del Plata, Mar del Plata (Argentina)*

**Alda Navaza**
*Faculté de Pharmacie, Université de Paris-Sud, Paris (France)*

**José A. Olabe***
*Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II, Ciudad Universitaria, 1428 Capital Federal (Argentina)*

and **Graciela E. Rigotti**
*Laboratorio de Cristalografía, Departamento de Física, Universidad Nacional de la Plata, La Plata (Argentina)*

(Received March 15, 1990; revised August 17, 1990)

## Abstract

The crystal structures of sodium hexacyanoosmate, ruthenate and ferrate decahydrates, $Na_4M(CN)_6 \cdot 10H_2O$ (M = Os, Ru, Fe), have been determined from X-ray diffraction data and refined by full matrix least-squares to final agreement values: $R = 0.038$, $R_w = 0.039$; $R = 0.026$, $R_w = 0.041$; $R = 0.060$, $R_w = 0.043$ for Os, Ru and Fe compounds, respectively. The compounds are isostructural and crystallize in the monoclinic space group $P2_1/n$, $Z = 2$, with $a = 9.154$, $b = 11.506$, $c = 9.876$ Å, $\beta = 97.95°$; $a = 9.146$, $b = 11.486$, $c = 9.867$ Å, $\beta = 98.00°$; $a = 9.038$, $b = 11.450$, $c = 9.782$ Å, $\beta = 97.57°$, for Os, Ru and Fe compounds, respectively. The structure can be described as layers of hexacyanometallate anions, intercalated with layers of sodium polyhedra containing hydration water molecules and N atoms, perpendicular to the crystallographic *ac* plane. Metal–C and C–N distances for the hexacyanide anions are correlated with those from other structurally related moieties. The infrared spectra of the compounds are complementary with previous results for potassium salts.

## Introduction

The study of metal–cyanide complexes is a matter of current interest [1]. In particular, much attention has been given to the behaviour of mixed-cyanide complexes of the $[Fe(CN)_5L]^{n-}$ series [2], where L may be a member of a vast group of ligands. Structure–reactivity correlations have been shown for various L, and for the Fe(II) and analogous Ru(II) complexes [3]. Systematic electron transfer studies on the influence of electron donor (acceptor) species have also been reported [4].

In this context, the scarce amount of information on osmium–cyanide complexes is remarkable [1]. The fragmentary spectroscopic data and the lack of structural studies on osmium–cyanide compounds [1] contrasts with the fascinating chemistry now being actively developed for the $[Os(NH_3)_5L]^{n-}$ complexes by Taube and coworkers [5].

As a part of a program to study the chemistry of Os(II) and Os(III) cyanide and substituted-cyanide complexes, we now report a crystal and molecular structure study of $Na_4Os(CN)_6 \cdot 10H_2O$. Although the sodium salts of the hexacyanometalate ions are less common than their potassium counterparts [1], two considerations determined our choice: (i) the existing crystallographic data on $K_4M(CN)_6 \cdot 3H_2O$ show that these substances are dimorphic [6]; (ii) a complete structural study is already available for $Na_4Fe(CN)_6 \cdot 10H_2O$ [7].

We also considered it valuable to extend our investigation to the isostructural ruthenium(II) analogue and to revisit the structure of the iron(II) compound, in order to obtain a consistent set of data for a series of sodium hexacyano-metalate(II) complexes. A correlation of the structural results with the infrared spectra is also included.

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

TABLE 1. X-ray data collection parameters and structural refinement for sodium hexacyanometalate compounds

| | M | | |
|---|---|---|---|
| | Os | Ru | Fe |
| Crystal colour | pale yellow | pale yellow | yellow |
| Crystal size ($\mu$m) | $150 \times 200 \times 200$ | $125 \times 300 \times 400$ | $75 \times 75 \times 300$ |
| $\mu$ (Mo K$\alpha$) (cm$^{-1}$) | 63.3 | 8.8 | 8.9 |
| Corrections | background, Lorentz and polarization | | |
| Absorption corrections | empirical (DIFABS, SDP Computing Programs) | | |
| Transmission factors min.; max. (%) | 0.894; 1.112 | 0.892; 1.137 | 0.877; 1.098 |
| Space group | $P2_1/n$ | | |
| $a$ (Å) | 9.144(2) | 9.146(3) | 9.038(2) |
| $b$ (Å) | 11.473(1) | 11.486(2) | 11.450(2) |
| $c$ (Å) | 9.859(2) | 9.867(2) | 9.782(3) |
| $\beta$ (°) | 97.93(2) | 97.99(3) | 97.57(3) |
| $Z$ | 2 | 2 | 2 |
| $\delta_{calc}$ (g cm$^{-3}$) | 1.99 | 1.71 | 1.60 |
| $\delta_{exp}$ (g cm$^{-3}$) | 1.98 | 1.73 | 1.57 |
| Diffractometer | Enraf Nonius CAD 4 | | |
| Monochromator | graphite | | |
| Radiation | Mo K$\alpha$ ($\lambda = 0.71069$ Å) | | |
| Temperature (°C) | 20 | | |
| Scan type | $\omega/2\theta$ | | |
| Scan range (°C) | $0.90 + 0.34$ tg $\theta$ | $0.80 + 0.35$ tg $\theta$ | $0.80 + 0.35$ tg $\theta$ |
| $2\theta$ range (°) | 2–25 | 2–25 | 2–22 |
| Scan speed (° min$^{-1}$) | depending upon reflection | | |
| Background | depending upon reflection; half of scan time in fixed position, before and after every scan | | |
| Standard reflections | $(52\bar{3})$<br>$(\bar{4}1\bar{1})$<br>$(\bar{3}\bar{1}\bar{2})$ | $(52\bar{3})$<br>$(161)$<br>$(\bar{4}1\bar{1})$ | $(52\bar{3})$<br>$(\bar{4}1\bar{1})$<br>$(\bar{3}\bar{1}\bar{2})$ |
| Variation of standards (%) | $<0.2$ | $<0.25$ | $<0.3$ |
| Reflections measured | 2 octants<br>$hkl$, $\bar{h}kl$<br>$-10<h<10$<br>$0<k<13$<br>$0<l<11$ | 2 octants<br>$hkl$, $\bar{h}kl$<br>$-10<h<10$<br>$0<k<11$<br>$0<l<13$ | 2 octants<br>$hkl$, $hk\bar{l}$<br>$0<h<8$<br>$0<k<12$<br>$-10<l<10$ |
| Reflections collected | 2028 | 2020 | 1381 |
| Unique reflections | 1908 | 1918 | 1191 |
| Reflections kept for refinement, ($I > 3\sigma(I)$ in the three cases) | 1210 | 1866 | 503 |
| Computing program | SDP, ref. 9 | | |
| Atomic form factors | ref. 10 | | |
| Minimized function | $\Sigma w(\|F_o\| - \|F_c\|)^2$ | | |
| Refined extinction coefficient | $1.20 \times 10^{-6}$ | $1.75 \times 10^{-6}$ | not refined |
| Weighting scheme | unit weights for all observed reflections (Os); statistical weights plus a factor to down weight intense reflections (Ru,Fe)[a] | | |
| Error of an observation of unit weight | 2.36 | 0.999 | 2.572 |
| Maximum shift/e.s.d. | 0.05 | 0.04 | 0.06 |
| No. parameters varied | 125 | 125 | 54 |
| $R$ | 0.023 | 0.026 | 0.060 |
| $R_w$ | 0.031 | 0.041 | 0.043 |
| $F(000)$ | 596 | 532 | 496 |

[a] Weighting scheme used is $w = 4(F_o)^2/[\Sigma(F_o)^2]^2$ with $[\Sigma(F_o)^2]^2 = [S^2(C + R^2B) + P(F_o)^2]^2/Lp^2$ where $S^2$ is the scan rate squared: $C$ is the total integrated peak count; $R^2$ is the ratio squared of scan time to background counting rate; $B$ is the total background count; $Lp$ is the Lorentz polarization factor, and the parameter $P$ is an experimental instability factor introduced to down weight intense reflections; 0–0.30 in both cases.

## Experimental

Crystals of $Na_4Os(CN)_6 \cdot 10H_2O$ were obtained by dissolving 1 g of $OsO_4$ (AESAR) in 50 ml of NaOH (1 M), with further addition of excess NaCN, up to the formation of a colourless solution. The latter was concentrated to a few ml in a rotavap at room temperature, in the dark; prismatic yellowish crystals were obtained by cooling the concentrated solution at −5 °C, and were dried under $CaCl_2$ in a dessicator.

Single crystals of $Na_4Fe(CN)_6 \cdot 10H_2O$ and $Na_4Ru(CN)_6 \cdot 10H_2O$ were obtained by recrystallization from aqueous solution mixtures of the respective potassium salts with NaCl [8].

A summary of X-ray data collection parameters and structural refinement for each one of the substances is given in Table 1. Cell parameters were obtained from setting angles of 25 reflections ($7° < 2\theta < 15°$) in the three cases.

The initial position for the Fe(Ru, Os) atom was obtained from MULTAN 78 [11]. The positions for N, C, and O (water oxygen) were obtained from subsequent difference Fourier maps.

Hydrogen atoms were located from a difference Fourier map as concentration of electronic density near oxygen atoms, only for the Ru compound, but their positions were not considered, in view of the rather distorted OW–H distances and H–OW–H angles.

Atomic parameters are presented in Table 2 for each one of the substances. Calculations were performed on a VAX computer.

IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer, with the aid of KBr disks.

## Results and discussion

An ORTEP [12] drawing of the osmium compound is shown in Fig. 1. The Os (Fe, Ru) atom is located on a symmetry centre, and the anion shows a rather distorted octahedral configuration, with bond lengths and angles (for each one of the compounds) displayed in Table 3.

The structure can be described as layers composed of hexacyanometalate anions, intercalated with layers containing sodium ions and hydration water molecules, both perpendicular to the crystallographic *ac* plane (Fig. 2).

Sodium polyhedra are packed conforming sets each one composed of four Na octahedra (Fig. 3). Each set contains two kinds of non-equivalent octahedra: A (sharing two edges) and B (sharing three edges) [13]. Symmetry-related sets are interlinked along the crystallographic *b* axis, through OW(5). The Na ions are located on the (111) planes of the cubes so formed.

TABLE 2. Positional parameters with e.s.d.s[a]

| Atom[b] | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| $Na_4[Os(CN)_6] \cdot 10H_2O$ | | | | |
| Os | 0.500 | 0.500 | 0.000 | 1.425(5) |
| C(1) | 0.5254(5) | 0.6786(6) | 0.0010(5) | 1.7(1) |
| C(2) | 0.7098(7) | 0.4809(4) | −0.0455(7) | 1.8(1) |
| C(3) | 0.4260(6) | 0.5121(4) | −0.2011(6) | 1.5(1) |
| N(1) | 0.5318(6) | 0.7754(5) | −0.0029(5) | 3.1(1) |
| N(2) | 0.8280(6) | 0.4693(5) | −0.0722(6) | 2.4(1) |
| N(3) | 0.3855(8) | 0.5188(4) | −0.3163(7) | 3.1(1) |
| Na(1) | 0.5103(3) | 0.1405(2) | 0.5940(3) | 3.10(6) |
| Na(2) | 0.5992(3) | −0.1272(2) | 0.7836(3) | 2.82(5) |
| OW(1) | 0.8149(6) | 0.2293(5) | 0.1127(8) | 6.2(2) |
| OW(2) | 0.2980(7) | 0.5096(4) | 0.3916(6) | 4.2(1) |
| OW(3) | 0.9448(5) | 0.4601(5) | 0.3014(5) | 3.3(1) |
| OW(4) | 0.8987(6) | 0.7212(4) | 0.1165(6) | 3.9(1) |
| OW(5) | 0.2141(6) | 0.2815(5) | 0.2662(6) | 4.6(1) |
| $Na_4[Ru(CN)_6] \cdot 10H_2O$ | | | | |
| Ru | 0.500 | 0.500 | 0.000 | 1.083(6) |
| C(1) | 0.5236(3) | 0.6761(3) | 0.0010(2) | 1.55(5) |
| C(2) | 0.7083(3) | 0.4811(2) | −0.0441(3) | 1.42(5) |
| C(3) | 0.4258(4) | 0.5108(2) | −0.2010(4) | 1.72(6) |
| N(1) | 0.5335(3) | 0.7758(3) | −0.0033(2) | 2.92(6) |
| N(2) | 0.8266(3) | 0.4705(2) | −0.0717(3) | 2.12(5) |
| N(3) | 0.3854(4) | 0.5193(2) | −0.3175(3) | 2.78(6) |
| Na(1) | 0.5107(1) | 0.1411(1) | 0.5942(1) | 2.74(2) |
| Na(2) | 0.5997(1) | −0.1275(1) | 0.7837(1) | 2.39(2) |
| OW(1) | 0.8180(3) | 0.2289(2) | 0.1120(3) | 5.66(8) |
| OW(2) | 0.2982(3) | 0.5098(2) | 0.3908(3) | 3.94(6) |
| OW(3) | 0.9450(2) | 0.4612(2) | 0.3004(2) | 2.68(4) |
| OW(4) | 0.8999(2) | 0.7200(2) | 0.1158(2) | 3.57(5) |
| OW(5) | 0.2140(3) | 0.2793(2) | 0.2650(2) | 3.90(5) |
| $Na_4[Fe(CN)_6] \cdot 10H_2O$ | | | | |
| Fe | 0.500 | 0.500 | 0.000 | 1.45(4) |
| C(1) | 0.520(1) | 0.6646(9) | 0.002(1) | 1.7(2) |
| C(2) | 0.700(1) | 0.483(1) | −0.0418(9) | 1.7(2) |
| C(3) | 0.432(1) | 0.506(2) | −0.1899(9) | 2.2(2) |
| N(1) | 0.5343(9) | 0.7659(8) | 0.000(1) | 2.3(2) |
| N(2) | 0.8211(9) | 0.4698(8) | −0.0708(8) | 2.1(2) |
| N(3) | 0.3897(9) | 0.5183(9) | −0.3090(8) | 2.5(2) |
| Na(1) | 0.5103(5) | 0.1399(4) | 0.5933(5) | 3.0(1) |
| Na(2) | 0.6015(5) | −0.1287(4) | 0.7860(5) | 2.8(1) |
| OW(1) | 0.816(1) | 0.2263(8) | 0.118(1) | 5.6(3) |
| OW(2) | 0.3032(8) | 0.510(1) | 0.3958(7) | 3.8(2) |
| OW(3) | 0.9432(8) | 0.4622(7) | 0.3063(7) | 3.0(2) |
| OW(4) | 0.8980(9) | 0.7219(7) | 0.1180(8) | 3.3(2) |
| OW(5) | 0.2145(9) | 0.2818(8) | 0.2672(8) | 4.0(2) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$. [b] Our nomenclature (1st number) corresponds to Vannerberg's atomic nomenclature [7] (2nd number) as follows: N(3), N(1); N(1), N(2); N(2), N(3); OW(3), O(1); OW(2), O(2); OW(5), O(3); OW(4), O(5).

Sodium–nitrogen and sodium–oxygen distances within each octahedra, together with Na–Na distances, are presented in Table 4. It may be observed

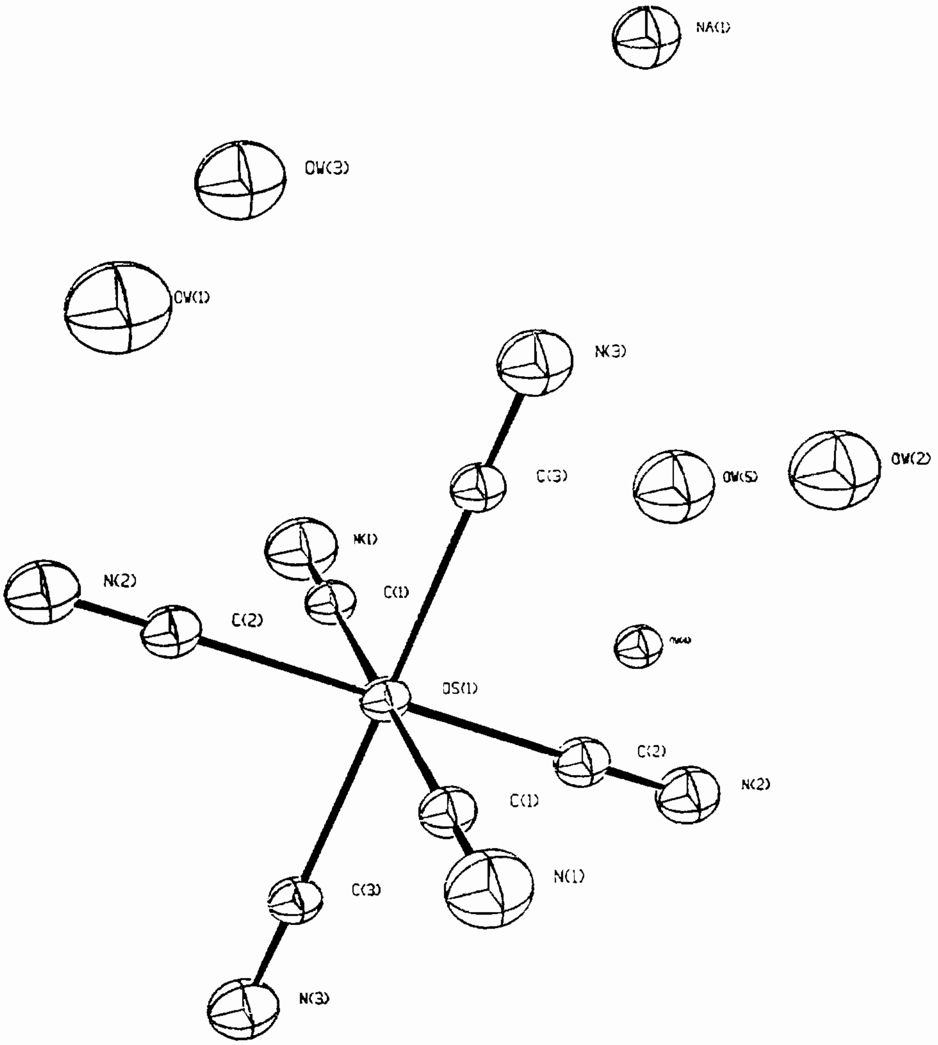

Fig. 1. ORTEP plot of $Na_4Os(CN)_6 \cdot 10H_2O$.

TABLE 3. Selected bond distances (Å) and angles (°) in $Na_4M(CN)_6 \cdot 10H_2O$

| M = Os | | M = Ru | | M = Fe | |
|---|---|---|---|---|---|
| Os–C(1) | 2.068(7) | Ru–C(1) | 2.035(3) | Fe–C(1) | 1.89(2) |
| Os–C(2) | 2.044(7) | Ru–C(2) | 2.023(3) | Fe–C(2) | 1.916(9) |
| Os–C(3) | 2.013(6) | Ru–C(3) | 2.010(3) | Fe–C(3) | 1.879(9) |
| C(1)–N(1) | 1.116(9) | C(1)–N(1) | 1.151(4) | C(1)–N(1) | 1.17(1) |
| C(2)–N(2) | 1.156(9) | C(2)–N(2) | 1.158(5) | C(2)–N(2) | 1.18(1) |
| C(3)–N(3) | 1.149(9) | C(3)–N(3) | 1.161(4) | C(3)–N(3) | 1.19(1) |
| C(1)–Os–C(2) | 90.0(2) | C(1)–Ru–C(2) | 90.3(1) | C(1)–Fe–C(2) | 90.7(4) |
| C(1)–Os–C(3) | 87.7(2) | C(1)–Ru–C(3) | 87.9(9) | C(1)–Fe–C(3) | 89.6(8) |
| C(2)–Os–C(3) | 89.4(2) | C(2)–Ru–C(3) | 89.7(1) | C(2)–Fe–C(3) | 89.3(4) |
| Os–C(1)–N(1) | 176.2(4) | Ru–C(1)–N(1) | 177.3(3) | Fe–C(1)–N(1) | 178.1(9) |
| Os–C(2)–N(2) | 179.3(5) | Ru–C(2)–N(2) | 178.8(2) | Fe–C(2)–N(2) | 177.7(9) |
| Os–C(3)–N(3) | 179.1(6) | Ru–C(3)–N(3) | 178.3(3) | Fe–C(3)–N(3) | 175.0(2) |

Numbers in parentheses are e.s.d.s in the least significant digits.

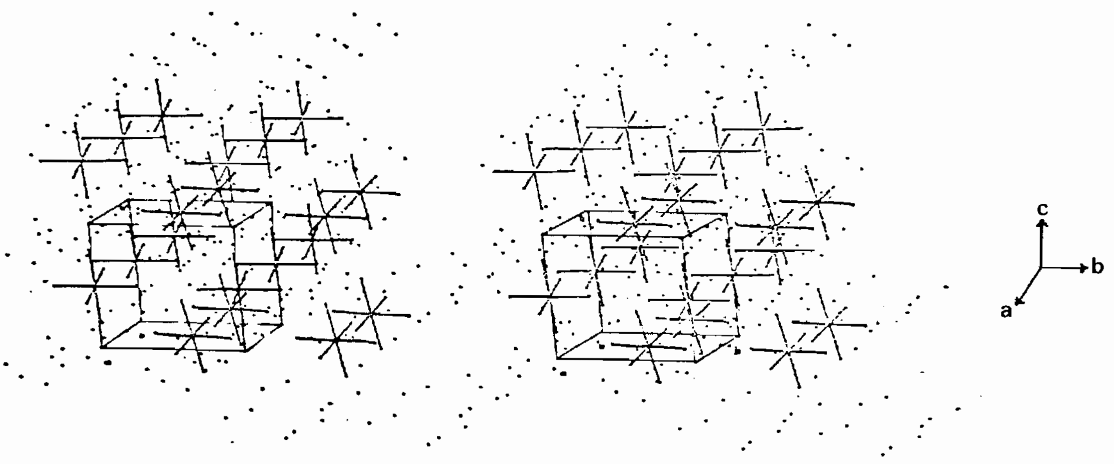

Fig. 2. Stereoview of the unit cell of the title compound.

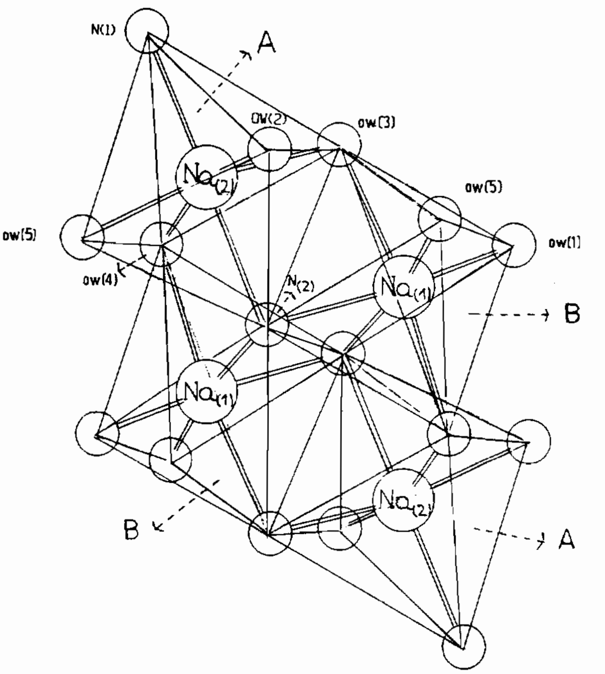

Fig. 3. Ordering of sodium polyhedra in $Na_4M(CN)_6 \cdot 10H_2O$ (M:Fe, Ru, Os).

that N(2) type atoms coordinate to three Na ions, N(1) to one Na, whilst N(3) are not coordinated to Na.

The hydrogen-bond scheme is inferred from oxygen(water)–acceptor distances. It may be described as zigzag chains of weakly hydrogen-bonded atoms along the crystallographic *a* axis, and ramificated along the *b* axis. OW–acceptor distances are displayed in Table 5 for each of the compounds.

TABLE 4. Bond distances associated to Na polyhedra (Å) (see Fig. 3)

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|
| $Na_4[Os(CN)_6] \cdot 10H_2O$ | | | | | |
| Na(1) | Na(1) | 3.720(4) | Na(1) | OW(5) | 2.511(6) |
| Na(1) | Na(2) | 3.638(3) | Na(2) | N(1) | 2.538(7) |
| Na(1) | Na(2) | 3.728(5) | Na(2) | N(2) | 2.534(7) |
| Na(1) | N(2) | 2.513(6) | Na(2) | OW(2) | 2.397(6) |
| Na(1) | N(2) | 2.491(6) | Na(2) | OW(3) | 2.408(6) |
| Na(1) | OW(1) | 2.360(6) | Na(2) | OW(4) | 2.535(6) |
| Na(1) | OW(3) | 2.497(7) | Na(2) | OW(5) | 2.559(6) |
| Na(1) | OW(4) | 2.521(7) | | | |
| $Na_4[Ru(CN)_6] \cdot 10H_2O$ | | | | | |
| Na(1) | Na(1) | 3.728(2) | Na(1) | OW(5) | 2.503(3) |
| Na(1) | Na(2) | 3.641(2) | Na(2) | N(1) | 5.524(3) |
| Na(1) | Na(2) | 3.728(2) | Na(2) | N(2) | 2.548(3) |
| Na(1) | N(2) | 2.529(3) | Na(2) | OW(2) | 2.390(3) |
| Na(1) | N(2) | 2.489(3) | Na(2) | OW(3) | 2.396(3) |
| Na(1) | OW(1) | 2.335(3) | Na(2) | OW(4) | 2.524(2) |
| Na(1) | OW(3) | 2.494(3) | Na(2) | OW(5) | 2.530(3) |
| Na(1) | OW(4) | 2.501(3) | | | |
| $Na_4[Fe(CN)_6] \cdot 10H_2O$ | | | | | |
| Na(1) | Na(1) | 3.680(7) | Na(1) | OW(5) | 2.505(9) |
| Na(1) | Na(2) | 3.644(7) | Na(2) | N(1) | 2.56(2) |
| Na(1) | Na(2) | 3.718(7) | Na(2) | N(2) | 2.57(1) |
| Na(1) | N(2) | 2.52(1) | Na(2) | OW(2) | 2.42(1) |
| Na(1) | N(2) | 2.51(1) | Na(2) | OW(3) | 2.41(1) |
| Na(1) | OW(1) | 2.37(2) | Na(2) | OW(4) | 2.535(9) |
| Na(1) | OW(3) | 2.531(9) | Na(2) | OW(5) | 2.52(1) |
| Na(1) | OW(4) | 2.51(1) | | | |

Numbers in parentheses are e.s.d.s in the least significant digits.

The analysis of the data on bond lengths and angles (Table 3) leads to the following conclusions.

1. Our results for the iron compound are in close agreement with the original work of Tullberg and

TABLE 5. Water contact distances (Å) in $Na_4M(CN)_6 \cdot 10H_2O$, (M = Os, Ru, Fe), with e.s.d.s in parentheses

| Distance | Os | Ru | Fe |
|---|---|---|---|
| OW(1)–N(3) | 2.989(8) | 2.978(4) | 2.945(14) |
| OW(2)–OW(5) | 2.958(8) | 2.980(4) | 2.964(14) |
| OW(2)–N(3) | 2.887(9) | 2.880(4) | 2.892(10) |
| OW(2)–N(3) | 3.106(10) | 3.096(5) | 3.025(11) |
| OW(3)–N(1) | 2.899(8) | 2.911(4) | 2.929(12) |
| OW(3)–N(3) | 3.057(9) | 3.058(4) | 3.021(11) |
| OW(4)–N(3) | 3.070(7) | 3.072(4) | 3.062(13) |

Vannerberg [7]. The mean distances for Fe–C and C–N are also quite similar to those obtained in a neutron-diffraction study of $K_4Fe(CN)_6 \cdot 3H_2O$ [14].

2. The data for $Na_4Ru(CN)_6 \cdot 10H_2O$ are also in reasonable agreement with those for $Mn_2Ru(CN)_6 \cdot 8H_2O$ [15]. The spread in Ru–C distances is larger in the sodium salt, but the mean Ru–C distance (2.023(3) Å) is very close to that found in the manganese salt (2.028(6) Å). In the latter compound Ru–C–N–Mn units are present in a three-dimensional array, all the cyano groups being present as ambidentate ligands; binuclear entities of the type $Mn_2N_6(H_2O)_4$ can be defined, with manganese octahedra showing a Mn–Mn distance of 3.705(1) Å. The distribution of Na octahedra in the sodium salts is more complex, as described above; three Na–Na distances can be defined (Table 5). The average Na–Na distance is of the same order (mean 3.7 Å) as the Mn–Mn distance; a significant difference, however, is shown by the longer N–Na distance (mean 2.52 Å) compared to the N–Mn distance (mean 2.15 Å), a result which seems reasonably consistent with the difference in cationic radii and with the higher polarizing influence of the Mn ion. The mean C–N distances in the sodium and manganese salts are also coincident (1.157(4) Å) and (1.160(8) Å), respectively.

The value of the Ru–C and C–N mean distances in $Na_4Ru(CN)_6 \cdot 10H_2O$ and $Na_2Ru(CN)_5NO \cdot 2H_2O$ [16] are 2.023(3), 2.056(4) Å (Ru–C) and 1.157(4), 1.143(4) Å (C–N), respectively. The differences are above the experimental error and seem to reflect the strong electron withdrawing influence of the NO ligand, with a corresponding lower $\pi$-backdonation from Ru(II) to cyanides [16, 17]. The latter effect is consistent with a weaker (longer) Ru–C bond and a stronger (shorter) C–N bond in the pentacyanonitrosyl complex as compared to the hexacyanide ion.

The infrared spectroscopic results are presented in Table 6. The assignment of bands is rather straightforward. A remarkable parallelism is observed in the different regions of the three spectra, as expected for isostructural compounds. In the high wavenumber region, a pattern of well defined peaks, assigned to O–H stretchings, appears, due to the differently hydrogen-bonded water (see above).

In the cyanide stretching region three strong peaks are observed in the Os and Ru compounds and two in the iron one (the band at 2058 $cm^{-1}$ is however broad and could be considered as an overlapping of two different modes).

The pattern seems to reflect the structural inequivalence of the three cyanide groups (see above), as only one stretching mode should be IR active in an isolated octahedron. Site symmetry effects and the coupling with lattice modes could also be responsible for the splitting of the C–N stretchings; two peaks have been measured in the potassium salts [18] and, interestingly, only one peak has been found in $Mn_2Ru(CN)_6 \cdot 8H_2O$, at 2077 $cm^{-1}$ [15]. In the latter substance, the cyanide groups are equivalent and the influence of Mn(II) coordination to the nitrile end seems to be determinant in the high value of $\nu$(CN), as compared to the potassium salt (2042 $cm^{-1}$). The perturbation of intramolecular vibrations by strong interionic forces has been discussed previously, through the comparison of the influence of $Mg^{2+}$ versus $Li^+$ in the vibrational stretching modes of the $Fe(CN)_6^{4-}$ ion [19]. The higher values reported here at 2067 and 2074 $cm^{-1}$ for the sodium salts of the osmium and ruthenium complexes, respectively, probably reflect the higher polarizing effect of Na ions on the cyanide groups; the corresponding values for the potassium salts are 2032 and 2042 $cm^{-1}$, respectively [18].

The differences of $\nu$(CN) for the three metal complexes, although significant, are however small, and could hardly be associated to a well defined $\sigma$–$\pi$ bonding scheme in the anions.

The intermediate region at *c.* 1620–1670 $cm^{-1}$ is characteristic of the water bending vibrations; here again, the splitted pattern may be associated to the complex hydrogen-bonded structure.

In the lower wavenumber region, below *c.* 700 $cm^{-1}$, a complex pattern of peaks protrude from a broad absorption background due to librational water modes; the bands at *c.* 550–590 $cm^{-1}$ may be reasonably assigned to the bending(s) of the M–C–N group(s), while the peaks at 369 (Os), 392 (Ru) and 430 (Fe) $cm^{-1}$ should correspond to the M–C stretching vibration. The latter assignment is consistent with Jones criteria [20] and with the expected influence of the atomic mass of the metal on the values of $\nu$(M–C).

TABLE 6. Infrared spectral wavenumbers ($cm^{-1}$)

| $Na_4Os(CN)_6 \cdot 10H_2O$ | $Na_4Ru(CN)_6 \cdot 10H_2O$ | $Na_4Fe(CN)_6 \cdot 10H_2O$ |
|---|---|---|
| 3596s | 3595s | 3589s |
| 3544s | 3546s | 3524s |
| 3485m | 3486m | 3487m |
| 3391s | 3404s | 3406s |
| 3286m | 3298m | 3300sh |
| 2067s | 2064s | 2058br |
| 2050s | 2060s | |
| 2023s | 2037s | 2025s |
| 2000sh | 2000sh | 1991sh |
| 1670w | 1670w | 1670w |
| 1649sh | 1650sh | 1650sh |
| 1637m | 1636m | 1637m |
| 1622sh | 1622sh | 1620sh |
| 716sh | 720w | |
| 647m | 635m | 650w |
| 558s | 552s | 589s |
| 544s | | |
| 504w | 480w | 479w |
| 450w | | |
| 407w | | 430m |
| 369m | 392m | 385w |

Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

## Supplementary material available

Listings of observed and calculated structure factors, anisotropic thermal parameters and root-mean-square amplitudes of thermal vibrations for osmium and ruthenium hexacyanide compounds are available from the authors on request.

## Acknowledgements

The authors thank Dr C. Dellavedova for running the IR spectra. G.R. is a member of the Scientific Staff of the Comisión de Investigaciones Científicas (Provincia de Buenos Aires). Financial support has been received from the latter Institution and from the Consejo Nacional de Investigaciones Científicas y Técnicas.

## References

1 A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals,* Academic Press, New York, 1976.
2 D. H. Macartney, *Rev. Inorg. Chem., 9* (1989) 101.
3 (a) F. M. Crean and K. Schug, *Inorg. Chem., 23* (1984) 853; (b) C. R. Johnson and R. E. Shepherd, *Inorg. Chem., 22* (1983) 1117, 2439; (c) J. A. Olabe, H. O. Zerga and L. A. Gentil, *J. Chem. Soc., Dalton Trans.,* 1267 (1987); (d) J. M. A. Hoddenbagh and D. H. Macartney, *Inorg. Chem., 25* (1986) 380, 2099.
4 (a) C. Creutz, *Prog. Inorg. Chem., 30* (1983) 1; (b) A. Haim, *Prog. Inorg. Chem., 30* (1983) 273; (c) T. J. Meyer, *Prog. Inorg. Chem., 30* (1983) 389; (d) N. Sutin, *Prog. Inorg. Chem., 30* (1983) 441.
5 (a) W. Dean Harman, M. Sekine and H. Taube, *J. Am. Chem. Soc., 110* (1988) 2439, and refs. therein; (b) H. Taube, *Pure Appl. Chem., 51* (1979) 901.
6 V. A. Pospelov and G. S. Zhdanov, *Zh. Fiz. Khim., 21* (1947) 405, 879; *Chem. Abstr., 41* (1947) 6790; *42* (1947) 2154.
7 A. Tullberg and N. G. Vannerberg, *Acta Chem. Scand., Ser. A, 28* (1974) 551.
8 G. G. Schlessinger, *Inorganic Laboratory Preparations,* Chemical Publishing Co., Inc., New York, 1962.
9 B. A. Frenz, *Enraf Nonius, Structure Determination Package, SDP Users Guide,* Enraf Nonius, Delft, The Netherlands, Apr. 1983.
10 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
11 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, *MULTAN 78,* a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York, U.K., and Louvain, Belgium, 1978.
12 C. K. Johnson, *ORTEP, Rep. ORNL-3794,* Oak Ridge National Laboratory, TN, 1965.
13 A. F. Wells, *Structural Inorganic Chemistry,* Clarendon, Oxford, 4th edn., 1975, p. 165, Fig. 5.8(h).

14 J. C. Taylor, M. H. Mueller and R. L. Hitterman, *Acta Crystallogr., Sect. A, 26* (1970) 559.

15 M. Rüegg, A. Ludi and K. Rieder, *Inorg. Chem., 10* (1971) 1773.

16 J. A. Olabe, L. A. Gentil, G. Rigotti and A. Navaza, *Inorg. Chem., 23* (1984) 4297.

17 R. F. Fenske and R. L. De Kock, *Inorg. Chem., 11* (1972) 437.

18 I. Nagakawa and T. Shimanouchi, *Spectrochim. Acta, 18* (1962) 101.

19 B. I. Swanson and J. J. Rafalko, *Inorg. Chem., 15* (1976) 249.

20 L. H. Jones, *Inorg. Chem., 2* (1963) 777.