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PREPARATION AND CHARACTERIZATION OF THE DICHROMATES OF THE ORGANIC BASES: 2,4′-BIPYRIDINE, 2,2′-DIPYRIDYLAMINE AND 4,4′-BIPYRIDINE

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Abstract—Dichromates of 2,4′-bipyridine (two forms), [(H_2-2,4′-bipy)(Cr_2O_7)] (**1**) and [(H-2,4′-bipy)$_2$(Cr_2O_7)] (**2**), 2,2′-dipyridylamine, [(H-dpam)$_2$(Cr_2O_7)] (**3**), and 4,4′-bipyiridine (two forms), [(H_2-4,4′-bipy)(Cr_2O_7)] (**4**) and [(H-4,4′-bipy)$_2$(H_2-4,4′-bipy)(Cr_2O_7)$_2$] (**5**), were prepared by reaction of chromium(VI) oxide with the free organic bases in the appropriate stoichiometric ratio in water at 25°C. The structures of compounds **2**, **3** and **4** were determined by X-ray crystallography and revealed the existence of discrete dichromate anions formed by two tetrahedral CrO_4 groups joined through shared O atoms, and the respective protonated organic bases hydrogen bonded to respective dinegative anions. A short C—H···O interaction [2.996(4) Å] between the organic cation and the dichromate anion was observed in compound **4**. All organic dichromates were also characterized by IR, UV–vis ^{1}H NMR measurements. For compounds **2**, **3** and **4**, a comparison was made and the crystallographic data of a series of mono- and polychromates and showed a correlation of the terminal and bridging Cr—O atomic distances with an increasing degree of polymerization. A graph theory cluster expansion was employed for these correlation studies.

A large number of dichromates of organic bases have been prepared and used as reagents in mild selective oxidation processes of organic substrates[1–4] as well as intermediates in the synthesis of new species of chromium in lower oxidation states.[5]

Chromates and polychromates of organic cations can be prepared: (i) by reaction of chromium(VI) oxide with an organic base in water or acetone–water media, (ii) by careful hydrolysis of the appropriate ester with the organic base in organic solvents and (iii) by reaction of alkaline dichromate (sodium or potassium dichromates) with the organic base hydrochloride in aqueous solution.[6,7]

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Whereas many structural studies of simple or double "inorganic" dichromates have been reported,[8-11] the same studies focusing mainly on dichromates of protonated organic bases are limited. Thus, in previous studies the structural characterizations have been reported by spectroscopic and X-ray powder diffraction data of pyridinium dichromates (two forms),[12] as well as trimethylpyridinium, isoquinolinium, methylquinolinium and 2,2′, 6′, 2″-terpyridinium dichromates.[13,14] Recently, Pressprich et al.[15] reported the preparation and structural characterization by X-ray diffraction analysis on a single crystal of bis(1H$^+$-pyrazinium N^4-oxide) dichromate, where the structure consists of dinegative dichromate anions hydrogen bonded to monopositive pyrazinium N-oxide cations. On the other hand, while the $Cr_2O_7^{2-}$ unit has a non-linear Cr—O—Cr angle (122–130°),[16] some angular $Mo_2O_7^{2-}$ structures have been found and at least one work has obtained a linear structure.[17] Moreover, the "organic" dichromates can present different formulae in accordance with the Cr : organic base ratio used in the synthesis.

The present paper deals with the preparation, spectroscopic and single-crystal X-ray characterization of new dichromates of protonated "bipyridinic" organic bases. All salts were prepared by reaction of chromium(VI) oxide, dissolved in water, with the respective free organic bases dissolved in acetone or water–acetone mixtures at 25°C in the appropriate stoichiometric relationship. Thus, when the CrO_3 : base stoichiometric ratio was 2 : 1 the dichromates with 2,4′-bipyridine, [(H_2-2,4′-bipy)(Cr_2O_7)] (**1**) and 4,4′-bipyridine, [(H_2-4,4′-bipy)(Cr_2O_7)] (**4**), were obtained. However, when the 1 : 1 CrO_3 : organic base ratio was employed, the "double" dichromate [(H-4,4′-bipy)$_2$(H_2-4,4′-bipy)(Cr_2O_7)$_2$](**5**) was obtained, whereas the dichromate with 2,4′-bipyridine, [(H-2,4′-bipy)$_2$(Cr_2O_7)] (**2**) was the sole isolated product. On the other hand, when the reaction was carried out using 1 : 1 and 2 : 1 CrO_3 : organic base stoichiometric ratios, only a dichromate with 2,2′-dipyridylamine, [(Hdpam)$_2$(Cr_2O_7)] (**3**), was isolated.

EXPERIMENTAL

Materials and apparatus

All starting materials were commercially available and used without further purification. Elemental analyses (C, H and N) were performed in a Carlo-Erba 1106 automatic analyser. IR spectra were obtained with a Nicolet 710FT-IR spectrophotometer in the 4000–250 cm^{-1} range using KBr pellets. Electronic spectra as diffuse reflectance were recorded on a Perkin–Elmer 550S spectrophotometer dispersing all samples in $BaSO_4$. ^{1}H NMR spectra were recorded at 297 K on a Bruker AC 200 spectrometer at 200 MHz, with tetramethylsilane as an internal standard after dilution of the sample in deuteriated dimethylsulphoxide.

Preparation of the compounds

[(H_2-2,4′-bipy)(Cr_2O_7)] (**1**). A concentrated solution of CrO_3 (1.0 g, 10 mmol) in water (1×10^{-2} dm^3) was added dropwise with stirring to a ice-cooled concentrated solution of 2,4′-bipyridine (0.78 g, 5 mmol) in acetone–water (1×10^{-2} dm^3, 4 : 1). A yellow precipitate was formed which was filtered through a fritted glass and washed with small amounts of cold water and acetone. The product was recrystallized from hot water and acicular orange crystals were obtained, then dried in dry air for a few hours and stored in a desiccator over $CaCl_2$ in the dark. Found : C, 32.1 ; H, 2.7 ; N, 7.4. $C_{10}H_{10}Cr_2N_2O_7$ requires : C, 32.1 ; H, 2.7 ; N, 7.5%.

[(H-2,4′-bipy)$_2$(Cr_2O_7)] (**2**). This compound was prepared as described above for **1** from CrO_3 (1.0 g, 10 mmol) and 2,4′-bipyridine (1.56 g, 10 mmol). The orange solid obtained was collected on a fritted glass funnel, washed twice with cold water and stored in a dessicator over $CaCl_2$ in the dark. Prismatic orange crystals were obtained upon recrystallization from hot water. Found : C, 45.4 ; H, 3.4 ; N, 10.6. $C_{20}H_{18}Cr_2N_4O_7$ requires : C, 45.3 ; H, 3.4 ; N, 10.6%.

[(Hdpam)$_2$(Cr_2O_7)] (**3**). This compound was prepared as for **1** using CrO_3 (1.0 g, 10 mmol) and 2,2′-dipyridylamine (1.70 g, 10 mmol). The orange solid obtained was collected on a fritted glass funnel, washed twice with a cold water–acetone mixture, dried in dry air and stored in a desiccator over $CaCl_2$. Prismatic orange crystals, suitable for X-ray work and very stable to air exposure, were obtained by recrystallization from hot water. Found : C, 42.7 ; H, 3.5 ; N, 14.8. $C_{20}H_{20}Cr_2N_6O_7$ requires : C, 42.9 ; H, 3.6 ; N, 15.0%. When the employed CrO_3 : organic base ratio was 2 : 1, orange crystals with the former composition were obtained.

[(H_2-4,4′-bipy)(Cr_2O_7)] (**4**). This compound was prepared in the same way as **1**, starting from CrO_3 (1.0 g, 10 mmol) and 4,4′-bipyridine (0.78 g, 5 mmol). The orange solid was collected by filtration, washed twice with a cold acetone–water mixture (1 : 1) and stored in a desiccator over $CaCl_2$ in the dark. Orange needle crystals were obtained upon recrystallization from hot water.

[(H-4,4′-bipy)$_2$($H_2$4,4′-bipy)(Cr_2O_7)$_2$] (**5**). This compound was prepared in the same way as **1** using the stoichiometric relationship CrO_3 : organic base (1 : 1). A concentrated solution of CrO_3 (1.0 g, 10 mmol) in water (1×10^{-2} dm^3) was added dropwise with stirring to an ice-cooled concentrated solution of 4,4′-bipyridine (1.56 g, 10 mmol) in acetone–water (2×10^{-2} dm^3, 4 : 1). A yellow precipitate was formed which was filtered through a fritted glass and washed with small amounts of cold water and acetone. The product was recrystallized from hot water and acicular yellow crystals were obtained, then dried in dry air and stored in a desiccator over $CaCl_2$ in the dark. Found: C, 39.9; H, 3.1; N, 9.5. Calc. for $C_{30}H_{28}Cr_4N_6O_{14}$: C, 39.8; H, 3.1; N, 9.3%.

Crystal structure determination and refinement

Table 1 gives details of crystal data, data collection and structure solution for compounds **2**, **3** and **4**.

[(H-2,4′-bipy)$_2$(Cr_2O_7)] (**2**). The determination of the lattice constants and the data collection were carried out on a computer-controlled diffractometer, Siemens R3m/V, employing Cu-K_α radiation in conjunction with balanced filters. The determination of the lattice parameters was based on the orientational parameters of 23 reflections in the range $6 \leqslant \theta \leqslant 28°$.

Intensities were measured using the ω-scan method with variable scan speed (8.0–29.5 min^{-1}) in the range $0 \leqslant \theta \leqslant 57°$. The intensities of two reflections, chosen as standard, were monitored every 80 reflections and did not decrease significantly. The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods[18] and refined by full-matrix least squares[19] on F. All the hydrogen atoms were located from ΔF syntheses and refined isotropically with a common factor. All non-hydrogen atoms were refined anisotropically.

[(Hdpam)$_2$(Cr_2O_7)] (**3**). Intensities were collected on a Phillips autodiffractometer, using graphite-monochromated Mo-K_α radiation by the ω–θ scan technique with a variable scan rate. Lattice parameters were calculated from 21 carefully centred reflections in the range $10 \leqslant \theta \leqslant 18.0°$.

Table 1. Crystal data, data collection and refinement parameters for **2**, **3** and **4**

	Compound **2**	Compound **3**	Compound **4**
Formula	$C_{20}H_{18}Cr_2N_4O_7$	$C_{20}H_{20}Cr_2N_6O_7$	$C_{10}H_{10}Cr_2N_2O_7$
Mr	530.38	560.41	374.19
λ(Å)	1.54178(Cu-K_α)	0.71069(Mo-K_α)	0.71069(Mo-K_α)
Space group	$P\bar{1}$	$P2_1/a$	*Pcmn*
a(Å)	8.072(3)	15.558(3)	5.053
b(Å)	10.658(2)	16.486(3)	12.320(2)
c(Å)	13.466(3)	8.885(2)	20.867(3)
α(°)	74.63(3)		
β(°)	82.74(3)	97.76(2)	
γ(°)	74.77(3)		
V(Å^3)	1075.8(5)	2258(1)	1299.0(4)
Z	2	4	4
D_c(g cm^{-3})	1.680	1.648	1.953
D_m(g cm^{-3})picnom.	1.66	1.67	1.92
μ(cm^{-1})	0.902(Cu-K_α)	10.63(Mo-K_α)	17.82(Mo-K_α)
F(000)	540	1144	752
Crystal dimensions (nm)	$1.00 \times 0.22 \times 0.30$	$0.70 \times 0.10 \times 0.20$	$0.10 \times 0.10 \times 0.15$
Reflections, total	2876	2134	1432
Reflections, observ.	2267[$I \geqslant 3\sigma(I)$]	1932[$I > 3\sigma(I)$]	1063[$I \geqslant 2.5\sigma(I)$]
R_{int}	0.033	0.018	
hkl range	−8,8;−11,11;0,14	−19,21;0,22;0,11	0,5;0,14;0,24
$(\Delta/\sigma)_{max}$	0.82	0.55	0.1
$\Delta\rho_{max}$(e Å^{-3})	0.93	0.91	0.4
$\Delta\rho_{min}$(e Å^{-3})	−0.56	−0.69	−0.4
Refined parameters	356	342	230
R	0.061	0.059	0.043
Rw			0.049
$w^{-1} = [\sigma^2(F)+gF^2]$	Unit	Unit	0.000049

The intensities were measured between (2θ) 3.5 and 59°. Two standard reflections were monitored every hour of X-ray exposure, the variation in the intensities of these reflections being <9.0%. The data were corrected for Lorentz and polarization effects; a profile analysis correction was applied but no absorption corrections were made. The structure was solved by direct methods[18] and refined by anisotropic full-matrix least-squares based[19] on F. The oxygen atom O(1) is disordered and this population converged to 0.80(2). The oxygen atoms at Cr(2) are also disordered, and the population converged to 62/38%. It became obvious during the analysis of the data that the [Hdpam]$^+$ cations were disordered over two sites (option A and option B, Table 3). The site occupancies refined to 0.80(2) (option A) and 0.20(2) (option B) for the major and minor sites in [Hdpam]$^+$ [N(1)–N(13)], 0.64(2) (option A) and [N(21) to N(33)] 0.36(2) (option B). Hydrogen atoms were positioned geometrically (C—H, 0.96 Å), except for those attached to the disordered positions, which were ignored.

[(H_2-4,4′-bipy) (Cr_2O_7)] (**4**). The determination of the lattice constants and the data collection were carried out on a computer-controlled Enraf–Nonius CAD-4 diffractometer employing Mo-K_α radiation in conjunction with a graphite monochromator. The determination of the lattice parameters was based on the orientational parameters of 25 reflections ($12 \leqslant \theta \leqslant 16°$).

The intensities were measured using the ω–2θ mode in the range $2 < \theta < 25°$. The observed reflections were subjected to Lorentz and polarization corrections, but no correction was made for absorption. The structure was solved by Patterson methods[18] and successive Fourier and least-squares methods.[19] The structure was refined first with isotropic and then with anisotropic thermal parameters. In the final stages of the refinement a Fourier difference synthesis revealed the locations of the hydrogen atoms, which were subsequently refined with isotropic thermal parameters. Atomic scattering factors for the three structures were obtained from International Tables for X-ray Crystallography.[20]

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen-atom coordinates, thermal parameters, remaining bond lengths and angles and observed and calculated structure factors.

RESULTS AND DISCUSSION

Fig. 1 shows a projection of the atomic arrangement and the geometry of the dichromate groups for compound **2**, as described in Table 2. Each chromium is surrounded by oxygen atoms in a tetrahedral arrangement. Thus, the terminal and bridging Cr—O bond distances are near the expected bond length average values, 1.60 and 1.76 Å, respectively, previously cited for other dichromates.[8,15] The non-bridging bond angles around Cr(1) are almost tetrahedral, 105.1(4)–111.4(3)°. Fig. 2 shows the crystal packing for compound **2**. The dichromate anions and the [H-2,4′-bipy]$^+$ cations are linked by hydrogen bonds. The nitrogen-to-oxygen distances are N(2)···O(3) [2.695(8) Å, $-x+1, -y+1, -z+1$] and N(4)···O(5) [2.836(11) Å, $-x+2, -y+1, -z+1$]. There are also some relatively short C—H···O interactions. The most significant carbon-to-oxygen distances are C(7)···O(7) [3.153(13)Å, x, $y-1$, z], C(8)···O(7) [3.199(14)Å, x, $y-1$, z] and C(19)···O(3) [3.068(18)Å, $-x+1, -y+1, -z+1$]. These interactions between oxygen atoms of the anions and the carbon atoms of the cations cannot

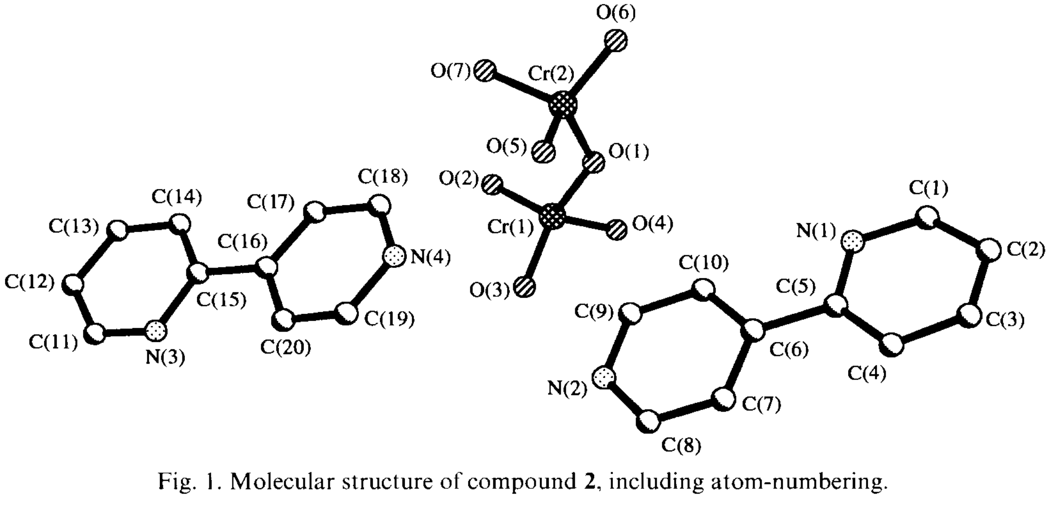

Fig. 1. Molecular structure of compound **2**, including atom-numbering.

Table 2. Selected bond lengths (Å) and selected bond angles in the dichromate anion for $[(H\text{-}2,4'\text{-bipy})_2(Cr_2O_7)]$(**2**) with estimated standard deviations (e.s.d.s.) in parentheses

In the dichromate anion			
Cr(1)—O(1)	1.775(7)	Cr(2)—O(1)	1.754(8)
Cr(1)—O(2)	1.590(6)	Cr(2)—O(5)	1.626(5)
Cr(1)—O(3)	1.626(5)	Cr(2)—O(6)	1.607(9)
Cr(1)—O(4)	1.596(7)	Cr(2)—O(7)	1.670(9)
In the [H-2,4′-bipy] cations			
N(1)—C(1)	1.330(11)	N(3)—C(11)	1.325(12)
N(1)—C(5)	1.344(9)	N(3)—C(15)	1.348(9)
N(2)—C(8)	1.325(12)	N(4)—C(18)	1.325(17)
N(2)—C(9)	1.338(11)	N(4)—C(19)	1.341(16)
C(1)—C(2)	1.378(14)	C(11)—C(12)	1.371(16)
C(2)—C(3)	1.363(12)	C(12)—C(13)	1.365(13)
C(3)—C(4)	1.360(12)	C(13)—C(14)	1.358(14)
C(4)—C(5)	1.378(10)	C(14)—C(15)	1.373(11)
C(5)—C(6)	1.484(10)	C(15)—C(16)	1.489(10)
C(6)—C(7)	1.393(10)	C(16)—C(17)	1.370(11)
C(6)—C(10)	1.382(11)	C(16)—C(20)	1.400(11)
C(7)—C(8)	1.359(12)	C(17)—C(18)	1.397(14)
C(9)—C(10)	1.373(12)	C(19)—C(20)	1.321(16)
Selected bond angles			
O(3)—Cr(1)—O(4)	111.4(3)	O(6)—Cr(2)—O(7)	106.4(5)
O(2)—Cr(1)—O(4)	109.5(4)	O(5)—Cr(2)—O(7)	108.0(4)
O(2)—Cr(1)—O(3)	109.1(3)	O(5)—Cr(2)—O(6)	114.7(4)
O(1)—Cr(1)—O(4)	107.6(3)	O(1)—Cr(2)—O(7)	105.1(4)
O(1)—Cr(1)—O(3)	109.6(4)	O(1)—Cr(2)—O(6)	111.3(5)
O(1)—Cr(1)—O(2)	110.3(4)	O(1)—Cr(2)—O(5)	110.7(4)
Cr(1)—O(1)—Cr(2)	135.3(5)		

be considered to be hydrogen bonds, but they do indicate some degree of polarization. The role of this type of interaction has been examined previously in chromium(VI) and molybdenum(VI) compounds with organic bases.[15,21–23]

The X-ray crystal structure of compound **3** is

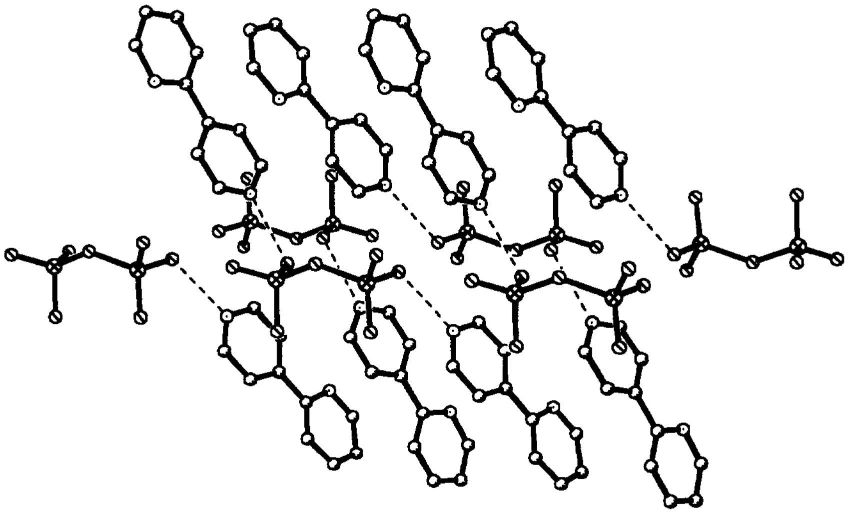

Fig. 2. Crystal packing of compound **2**. Hydrogen atoms are omitted for clarity.

shown in Fig. 3 (option A and option B), which includes the atom-numbering scheme. Significant bond lengths, bond angles and least-squares planes in the dichromate anion and dipyridylammonium cations are presented in Table 3. For this compound, bond distances and angles in the dichromate anion are similar to compound **2**. The crystal structure consists of dichromate anions and $[Hdpam]^+$ cations joined by intra- and intermolecular hydrogen-bond interactions. The most important nitrogen-to-oxygen observed distances are N(71)···O(3) [2.522(33) Å, $-x+1/2, y-1/2, -z+1$] and O(20)···N(271) [2.787(42) Å, $-x+1/2, y+1/2, -z+1$]. The dihedral angles formed between the pyridine rings, 4.6(3) and 5.6(3)°, indicate that the $[Hdpam]^+$ cations are not essentially co-planar. Furthermore, there are notable perturbations in the bonding patterns as is shown by high standard deviations.

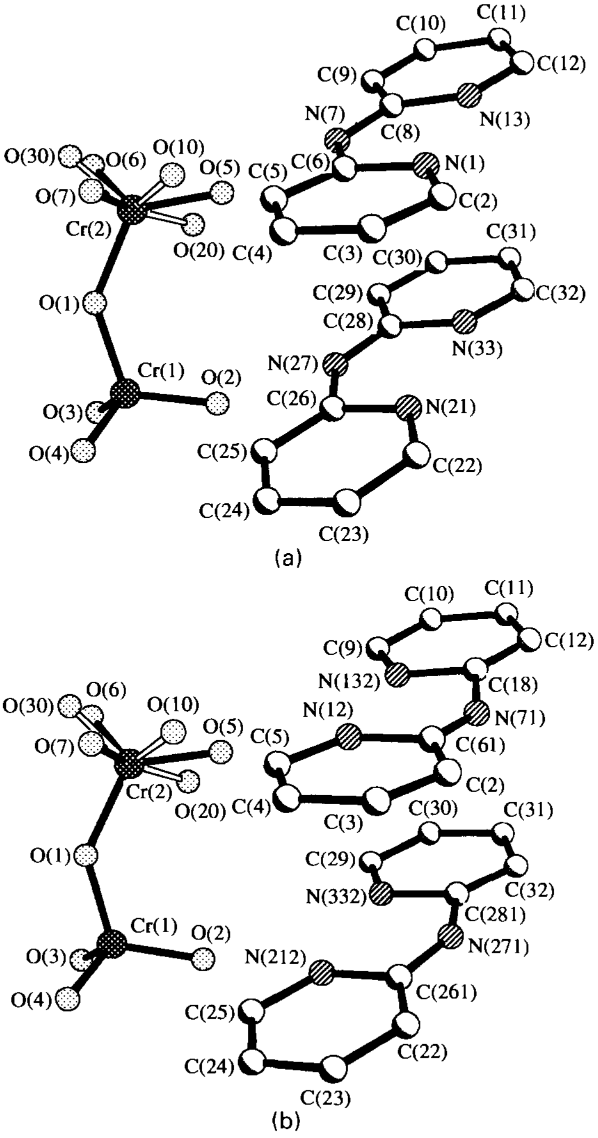

Fig. 3. Molecular structure of compound 3, including atom-numbering: (a) option A and (b) option B.

The X-ray crystal structure of compound **4** with the atom-numbering scheme is described in Fig. 4. In Table 4 the geometry, interatomic distances and bond angles are given together with the standard deviations. This structure consists of a dichromate anion and a 4,4′-bipyridinium dication with a crystallographic plane of symmetry. There are four crystallographically non-equivalent oxygen atoms, six carbon atoms, two nitrogen atoms and a chromium atom. Each chromium atom is surrounded by a slightly distorted tetrahedron of four oxygen atoms; the bond angles around the chromium atom are in the 105.9(1)–111.5(1)° range. Two tetrahedra share the O(1) atom forming a dichromate anion in an almost eclipsed conformation. The bridging angle Cr(1)—O(1)—Cr(1)*[$x, -y+3/2, z$] is 126.99(4)°, while the values for the same bridging angle in compounds **2** and **3** are 135.3(5) and 139(1)°, respectively. The two latter values are larger than that found in other works.[16] The terminal chromium–oxygen distances for **4** are from 1.593(3) to 1.608(2) Å and the Cr—O bridging bond length is 1.796(2)Å. This value is larger than that found for other bridging Cr—O bonds in a dichromate anion. However, Pressprich *et al.* found a value of 1.816(7) Å for a Cr—O bridging bond distance in the bis($1H^+$-pyrazinium N^4-oxide) dichromate.[15] The observed bond lengths for the compounds **2**, **3** and **4** permit a comparison with crystallographic data of mono- and polychromates in a correlation diagram on terminal and bridging Cr—O distances.[24] The values found for the terminal and bridging Cr—O distances are in the expected range for the dichromate anion. These chromium–oxygen distances may also be examined in terms of a cluster expansion:[24]

$$L(\Gamma) = \sum_{\gamma\in\Gamma} N(T,\gamma)l(\gamma),$$

where a graph-theoretical notation is used; L(Γ) is the length of terminal or bridging Cr—O bonds and the other symbols are cited in the literature.[24] The calculated values for terminal and bridging chromium–oxygen distances are 1.615 and 1.780 Å, respectively, and these are in good agreement with the observed bond distances.

The $[H_2\text{-}4,4'\text{-bipy}]^{2+}$ cations in **4** are essentially planar with negligible deviation from the best least-squares plane. The crystal packing of compound **4** is shown in Fig. 5. Dichromate anions are joined to $[H_2\text{-}4,4'\text{-bipy}]^{2+}$ dications by hydrogen bonds. There are N(8)···O(2) links that are part of a symmetric bifurcate N(8)—H···O(2) [$x+1, y, z$] and the N(8)—H···O(2)* [$x+1, -y+3/2, z$] hydrogen

Table 3. Selected bond distances (Å), angles (°) and least-squares planes for [(Hdpam)$_2$(Cr$_2$O$_7$)] (**3**) with estimated standard deviations (e.s.d.s.) in parentheses

Cr(1)—O(1)	1.72(1)
Cr(1)—O(2)	1.60(1)
Cr(1)—O(3)	1.59(1)
Cr(1)—O(4)	1.61(1)
Cr(2)—O(1)	1.73(1)
Cr(2)—O(5)	1.55(1)
Cr(2)—O(6)	1.54(3)
Cr(2)—O(7)	1.53(2)
Cr(2)—O(10)	1.49(3)
Cr(2)—O(20)	1.53(3)
Cr(2)—O(30)	1.53(4)

Option A		Option B	
N(1)—C(2)	1.37(1)	C(61)—C(2)	1.37(1)
N(1)—C(6)	1.36(1)	C(61)—N(12)	1.36(1)
C(5)—C(6)	1.37(2)	C(5)—N(12)	1.37(2)
C(6)—N(7)	1.36(1)	C(61)—N(71)	1.31(3)
N(7)—C(8)	1.37(2)	N(71)—C(81)	1.39(3)
C(8)—C(9)	1.38(2)	N(132)—C(9)	1.38(2)
C(8)—N(13)	1.35(1)	N(132)—C(81)	1.35(1)
C(12)—N(13)	1.33(1)	C(12)—C(81)	1.33(1)
N(21)—C(22)	1.36(1)	C(261)—C(22)	1.36(1)
N(21)—C(26)	1.36(1)	C(261)—N(212)	1.36(1)
C(25)—C(26)	1.35(2)	C(25)—N(212)	1.35(2)
C(26)—N(27)	1.36(1)	C(261)—N(271)	1.34(3)
N(27)—C(28)	1.32(1)	N(271)—C(281)	1.33(3)
C(28)—C(29)	1.39(1)	N(332)—C(29)	1.39(1)
C(28)—N(33)	1.36(1)	C(281)—N(332)	1.36(1)
C(32)—N(33)	1.33(2)	C(32)—C(281)	1.33(2)

O(3)—Cr(1)—O(4)	111(1)
O(2)—Cr(1)—O(4)	109(1)
O(2)—Cr(1)—O(3)	109(1)
O(1)—Cr(1)—O(4)	102(1)
O(1)—Cr(1)—O(3)	111(1)
O(1)—Cr(1)—O(2)	115(1)
O(20)—Cr(2)—O(30)	110(2)
O(10)—Cr(2)—O(30)	111(2)
O(10)—Cr(2)—O(20)	109(2)
O(6)—Cr(2)—O(7)	110(1)
O(5)—Cr(2)—O(7)	110(1)
O(5)—Cr(2)—O(6)	112(1)
O(1)—Cr(2)—O(30)	108(2)
O(1)—Cr(2)—O(20)	96(1)
O(1)—Cr(2)—O(10)	121(1)
O(1)—Cr(2)—O(7)	91(1)
O(1)—Cr(2)—O(6)	109(1)
O(1)—Cr(2)—O(5)	122(1)
Cr(1)—O(1)—Cr(2)	139(1)

continued overleaf

Table 3. *Continued.*

Option A		Option B	
C(2)—N(1)—C(6)	119(1)	C(2)—C(61)—N(12)	119(1)
N(1)—C(2)—C(3)	122(1)	C(61)—C(2)—C(3)	122(1)
C(4)—C(5)—C(6)	121(1)	C(4)—C(5)—N(12)	121(1)
N(1)—C(6)—C(5)	120(1)	C(61)—N(12)—C(5)	120(1)
C(5)—C(6)—N(7)	124(1)	C(61)—N(71)—C(81)	146(3)
N(1)—C(6)—N(7)	116(1)	N(71)—C(81)—C(12)	137(2)
C(6)—N(7)—C(8)	132(1)	N(71)—C(81)—C(8)	103(1)
N(7)—C(8)—N(13)	116(1)	N(12)—C(61)—N(71)	104(2)
N(7)—C(8)—C(9)	124(1)	C(2)—C(61)—N(71)	138(2)
C(9)—C(8)—N(13)	120(1)	C(9)—N(132)—C(81)	120(1)
C(8)—C(9)—C(10)	121(1)	N(132)—C(9)—C(10)	121(1)
C(11)—C(12)—N(13)	122(1)	C(11)—C(12)—C(81)	122(1)
C(8)—N(13)—C(12)	120(1)	N(132)—C(81)—C(12)	120(1)
C(22)—N(21)—C(26)	118(1)	C(22)—C(261)—N(212)	118(1)
N(21)—C(22)—C(23)	123(1)	C(261)—C(22)—C(23)	123(1)
C(24)—C(25)—C(26)	121(1)	C(24)—C(25)—N(132)	121(1)
N(21)—C(26)—C(25)	120(1)	C(261)—N(212)—C(25)	120(1)
C(25)—C(26)—N(27)	126(1)	C(261)—N(271)—C(281)	148(2)
N(21)—C(26)—N(27)	114(1)	N(271)—C(281)—C(32)	135(1)
C(26)—N(27)—C(28)	135(1)	N(271)—C(281)—C(28)	104(1)
N(27)—C(28)—N(33)	115(1)	N(212)—C(261)—N(271)	104(1)
N(27)—C(28)—C(29)	126(1)	C(22)—C(261)—N(271)	137(1)
C(29)—C(28)—N(33)	119(1)	C(29)—N(332)—C(281)	119(1)
C(28)—C(29)—C(30)	119(1)	N(332)—C(29)—C(30)	119(1)
C(31)—C(32)—N(33)	122(1)	C(31)—C(32)—C(281)	122(1)
C(28)—N(33)—C(32)	121(1)	N(332)—C(281)—C(32)	121(1)

Planes with deviations (Å)

Plane 1: Option A [Option B]

N(1) [C(61)] −0.0001, C(2) −0.0158, C(3) 0.0165, C(4) −0.0147, C(5) 0.0037, C(6) [N(12)] 0.0027

Plane 2: Option A [Option B]

C(8) [N(132)] −0.0010, C(9) −0.0001, C(10) −0.0016, C(11) 0.0037, C(12) −0.0053, N(13) [C(81)] 0.0024

Plane 3: Option A [Option B]

N(21) [C(261)] −0.0030, C(22) 0.0036, C(23) 0.0028, C(24) −0.0076, C(25) 0.0045, C(26) [N(212)] 0.0006

Plane 4: Option A [Option B]

C(28) [N(332)] −0.0041, C(29) −0.0045, C(30) 0.0095, C(31) −0.0027, C(32) −0.0087, N(33) [C(281)] 0.0091

Dihedral plane	Angles plane	Formed by LSQ-planes angle(e.s.d.)
1	2	5.6(3)
1	3	7.8(3)
1	4	3.8(3)
2	3	2.7(4)
2	4	3.5(3)
3	4	4.6(3)

bond with a N···O distance of 2.975(4) Å. The four atom configuration is not planar. Deviations from the mean N(8), H(8), O(2) and O(2)* plane are −0.25, 0.75 and 0.01 Å, respectively. Also, the N(3) atom is involved in another intermolecular hydrogen bond with N(3)···O(1) [2.670(5) Å, $-x-1/2$, y, $z+1/2$]. Furthermore, a significantly short C(2)···O(3) [2.996(4) Å, $x-1/2$, $y-1/2$, $-z+1/2$] interaction has been observed. This issue supports the idea of the existence of a significant C—H···O hydrogen bonding and it is comparable with the normal interactions involving O—H or N—H groups (2.3–2.9 Å). Perhaps this C—H···O interaction value is the shortest found in the litera-

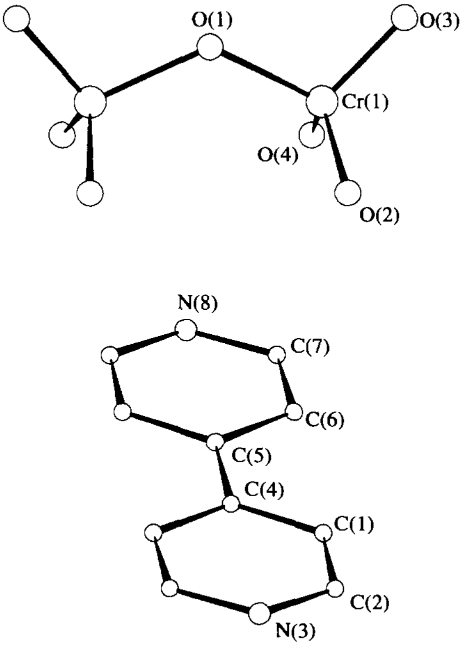

Fig. 4. Molecular structure with atom-numbering of compound **4**.

ture for any chromium(VI) compounds with organic bases.[15]

The IR spectra of all the compounds studied show bands in the same range, *ca* 3200–3000 cm^{-1}, corresponding to the stretching vibrations of C—H groups in pyridine-type compounds.[24] Equally, there are a complex series of absorptions between 2900 and 2100 cm^{-1} in all the spectra which are attributed to the stretching vibration of the $N—H^+$ "pyridinium" groups involved in intermolecular hydrogen bonding. The weak bands observed at *ca* 1200–1000 cm^{-1} in all spectra were assigned to in-plane C—H deformations and ring-breathing modes.[25,26] The IR spectra of all compounds contain the expected four types of frequencies assigned immediately to the Cr—O terminal and bridging bonds. Thus, all compounds exhibit bands in 560–540 and 770–740 cm^{-1} regions which belong to the symmetric and antisymmetric stretching modes of vibration of the Cr—O—Cr fragment (ν_2 frequency, symmetry A),[27] respectively. On the other hand, all spectra show frequencies in *ca* 900–880 and 955–930 cm^{-1} regions corresponding to the symmetric and antisymmetric Cr—O terminal bond stretching vibrations (ν_1 frequency, symmetry A),[27] respectively. Furthermore, all compounds exhibit a band in a *ca* 350 cm^{-1} region assigned to the bending mode of vibration of the Cr—O terminal bonds.[27]

The electronic diffuse reflectance spectra of all compounds show two bands, the first between *ca* 325 and 350 nm ($^6t_1 \rightarrow {}^5t_1e$) and the second between 435 and 440 nm (LMCT), corresponding to the dichromate anion. On the other hand, all spectra exhibit bands below 260 nm assigned to $^6t_1 \rightarrow {}^5t_1{}^1t_2$ transitions in the dichromate anion overlapping with the electronic transitions in the organic cations.[28]

Experimental IR and electronic spectra of the dichromate anions of this paper are in good agreement with the results of *ab initio* theoretical calculations for $M_2O_7^{2-}$ anions (M = Cr, Mo, W).[16]

Table 4. Selected bond distances (Å) and bond angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for $[(H_2\text{-}4,4'\text{-bipy})(Cr_2O_7)]$ (**4**)

(a) In the dichromate anion			
Cr(1)—O(1)	1.7956(16)	O(3)—Cr(1)—O(4)	110.3(1)
Cr(1)—O(2)	1.6084(24)	O(2)—Cr(1)—O(4)	109.5(1)
Cr(1)—O(3)	1.6060(23)	O(2)—Cr(1)—O(3)	111.5(1)
Cr(1)—O(4)	1.5925(30)	O(1)—Cr(1)—O(4)	109.7(1)
Cr(1)—O(1)	1.7956(16)	O(1)—Cr(1)—O(3)	105.9(1)
		O(1)—Cr(1)—O(2)	109.9(1)
		Cr(1)—O(1)—Cr(1)	126.99(4)
	Cr(1)····Cr(1)^i 3.214(1)^a		
(b) In the [4,4′-bipy] cation			
C(1)—C(4)	1.374(4)	C(2)—C(1)—C(4)	119.6(3)
C(2)—N(3)	1.317(4)	C(1)—C(2)—N(3)	120.5(3)
C(4)—C(5)	1.506(6)	C(1)—C(4)—C(5)	120.9(1)
C(5)—C(6)	1.380(4)	C(4)—C(5)—C(6)	120.7(1)
C(6)—C(7)	1.379(5)	C(5)—C(6)—C(7)	119.5(3)
C(7)—N(8)	1.324(4)	C(6)—C(7)—N(8)	120.4(3)
C(1)—C(2)	1.377(5)		

[a] Roman numeral scripts refer to the following equivalent position relative to x, y, z : i = x, $y+3/2$, z.

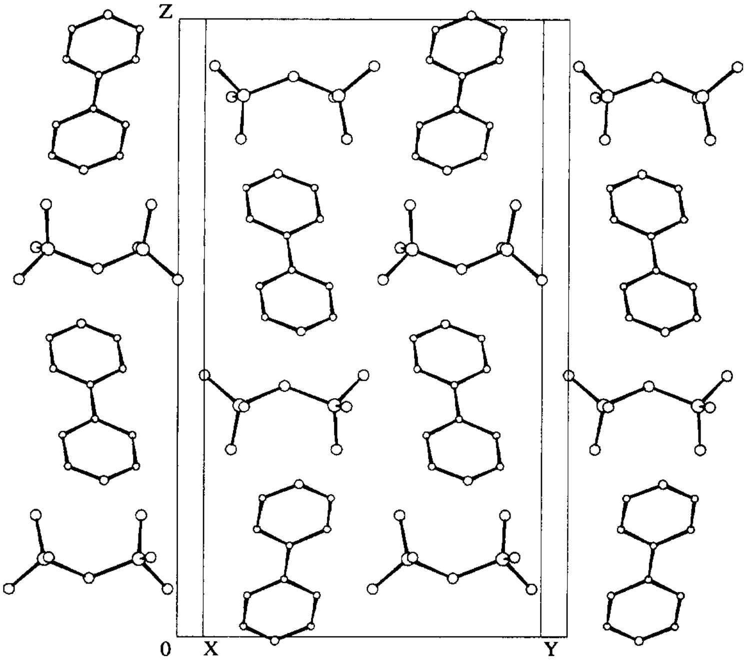

Fig. 5. Crystal packing of compound **4**. Hydrogen atoms are omitted for clarity.

Proton NMR measurements of the five organic dichromates reported in this paper have been obtained in DMSO-d_6 at room temperature. All spectra are very similar to those exhibited by the respective hydrochlorides of the organic bases. Thus, compounds **1** and **2** show broad multiplets in the aromatic proton region between $\delta = 8.6$ and $\delta = 7.4$ ppm. Furthermore, compound **1** exhibits two very sharp singlets at $\delta = 4.3$ and 1.1 ppm, respectively, suggesting the existence of two types of "pyridinium" protons involved in a very rapid exchange with the solvent. Compound **2** only presents a sharp singlet centred at $\delta = 1.2$ ppm, suggesting the existence of one type of "pyridinium" proton in this compound. In the case of compound **3** the ^{1}H NMR spectrum shows four resonances between $\delta = 8.3$ and $\delta = 7.1$ ppm, corresponding to the four protons of each pyridine ring. The NH resonance of the secondary amine group appears as a broad singlet in $\delta = 11$ ppm. The proton on the nitrogen atom of pyridine rings exchanges at a low rate; a very broad absorption can be observed at a downfield position between $\delta = 3.0$ and 4.0 ppm. Compound **4** shows two resonances centred at $\delta = 8.1$ ppm and $\delta = 7.9$ ppm, assigned to the aromatic protons, and a sharp singlet centred at $\delta = 1.04$, ppm assigned to the pyridinium proton. The integration of these signals shows a ratio of 4:4:2 in accordance with the proposed formula. On the other hand, compound **5** also exhibits two resonances at $\delta = 7.72$ and $\delta = 6.68$ ppm, assigned to the aromatic protons in pyridine rings. Furthermore, a sharp singlet at $\delta = 1.45$ ppm was observed and assigned to the pyridinium proton. The corresponding values of the integrals of these signals are in a 12:12:4 ratio, in accordance with the two types of 4,4′-bipyridine cations in the proposed formula.

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