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POTENTIAL MOLECULAR MATERIALS BASED ON ORGANIC–INORGANIC CHARGE-TRANSFER SALTS DERIVED FROM $[Mo_6O_{19}]^{2-}$ ISOPOLYOXOANION AND HEMICYANINE DYES: SYNTHESIS, SPECTRA PROPERTIES AND X-RAY STRUCTURE

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Abstract—The charge-transfer salts between a series of hemicyanine dyes and the hexamolybdate anion have been synthesized and characterized. Spectroscopic data support the presence of a sizeable electronic interaction between electron-rich aromatic organic and inorganic anions in the solid state. These complexes contain the $[\text{donor-}\pi\text{-cation}]_n^+[\text{polyoxoanion}]^{n-}$ structure. The bond length alternation (BLA) between single and double bonds are -0.09 and -0.10 for **1** and **3**, respectively. Hence, according to the relationship between BLA and hyperpolarizability (β), β ($\times 10^{-30}$ esu) values of 60 and 35 are obtained for complexes **1** and **3**, respectively. The cations form head-to-tail DADA stacks in these two salts, the polyoxoanion fits into the channel formed by the cation. The distances between pairs of stacks are 3.56 and 3.45 Å for **1** and **3**, respectively.

Recently there have been a number of reports in the literature[1–5] addressing charge-transfer complexes, which may constitute a range of molecular solids with novel structural, magnetic and transport properties, arising from organic donor and large quasispherical inorganic acceptors e.g. $(TTF)_3Mo_6O_{19}$. Polyoxoanions interact with organic molecules essentially by virtue of their acid–base properties, high electron-acceptor ability[6] and inducing the co-existence of mixed valence states in both the organic and inorganic systems.

By using the special properties of the polyoxoanion, our aim is to design and synthesize molecular materials with several applications in non-linear optics, using the photorefractive effect and other areas of molecular electronics. In order to synthesize these materials one of the important aspects of the development of truly reversible photochromic materials. Photochromism means a photoinducement of electron-transfer processes, which can produce charge separation, hyperpolarizability and change of refractive index. Our design strategy is to form a novel molecular material by taking the valence, variable polyoxoanions as inorganic acceptors, and those organic substances with non-linear optical properties as organic donors. For a reversible photochromism[7,8] as shown in eq. (1):

$$[\text{donor-}\pi\text{-cation}^+]_n[\text{polyoxoanion}]^{n-} \underset{\text{dark or } h\nu 2}{\overset{h\nu 1}{\rightleftharpoons}} [\text{donor}^{\delta+}\text{-}\pi\text{-cation}^+]_n[\text{polyoxoanion}]^{(n+\delta)-} \quad (1)$$

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we chose hemicyanine dyes (Scheme 1) as organic donors, as they have good optical properties, e.g. 4-*N*-methylstibazolium salts possess the largest SHG efficiency[9] to date, 1000 times urea and the largest electro-optic effect.[10]

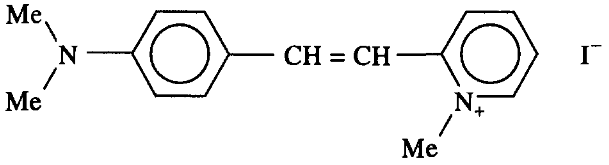
In this paper the synthesis, structural and spectroscopic characterization of some charge-transfer salts formed by the hexamolybdate anion and hemicyanine dyes are reported.

EXPERIMENTAL

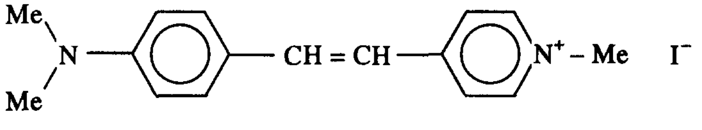
All reagents and materials were reagent grade and used without subsequent purification. Hemicyanine dyes and $[NBu_4]_2[Mo_6O_{19}]$ were synthesized according to the literature method.[11,12] IR spectra were recorded as KBr discs on a Nicolet 170 SX spectrophotometer. UV–vis spectra were recorded as MgO discs on a Shazidaz 240.

Preparation of complexes

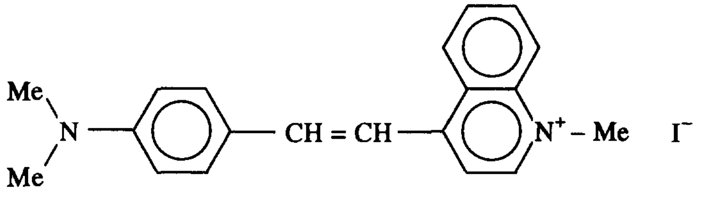
Metathesis reaction under acetonitrile solutions of $[NBu_4]_2[Mo_6O_{19}]$ with hemicyanine dyes, [2-(4-dimethylaminophenyl)ethenyl]pyridinium(2-DAPP) (**1**), [4-(4-dimethylaminophenyl)ethenyl] pyridinium (4-DAPP) (**2**) and [4-(4-dimethyl-



(2 – DAPP)I



(4 – DAPP)I



(DAPQ)I

Scheme 1.

aminophenyl)ethenyl]quinolinium (DAPQ) (**3**), respectively, in 1 : 2 molar ratio immediately gave insoluble, dark green microcrystalline powders [(**1**), (**2**) and (**3**)] which were washed by hot acetonitrile several times. Yield > 99%. Dark green, shiny cubic-like crystals suitable for X-ray studies were recrystallized from DMF. Found : C, 30.4 ; H, 3.5 ; N, 5.5. Calc. for **1** : C, 30.3 ; H, 3.5 ; N, 3.5%. Found: C, 28.5; H, 3.7; N, 4.3. Calc. for **2**: C, 28.3 ; H, 3.6 ; N, 4.1%. Found : C, 33.0 ; H, 2.9 ; N, 3.7. Calc. for **3** ; C, 32.9 ; H, 2.9 ; N, 3.8%.

Crystal structure determination

Crystals were mounted on a glass fibre. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.7107$ Å). The MSC/Rigaku TEXSAN 3.1 program package was used for the structure resolution on a MICRO VAX 3100 computer. Crystallographic data and additional details regarding data collection and refinement are given in Table 1. The empirical absorption correction by DIFABS was carried out. The positions of all molybdenum atoms were determined by Patterson methods, and the other non-hydrogen atoms were determined by Fourier syntheses. The positions of hydrogen atoms were calculated [d(C-H) = 0.95 Å] as a fixed contribution. The structures were refined by full matrix least squares. A weighting scheme $w = \sigma^{-2}(F)$ was applied. Bond lengths and angles of complex **1** are given in Tables 2 and 3 and of complex **3** in Tables 4 and 5.

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

Table 1. Crystallographic data for complexes **1** and **3**

	1	**3**
Formula	$C_{38}H_{52}Mo_6N_6O_{21}$	$C_{40}H_{42}Mo_6N_4O_{19}$
Formula weight	1504.50	1458.43
Temperature (K)	296	296
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	9.752(6)	9.319(5)
b (Å)	11.475(4)	19.637(6)
c (Å)	11.873(2)	12.465(7)
α (°)	104.06(2)	
β (°)	105.49(4)	96.19(4)
γ (°)	91.38(4)	
V (Å^3)	1236(1)	2268(2)
Z	1	2
$D_{calc.}$ (g cm^{-3})	2.02	2.14
F (000)	742	1428
Colour	Dark green	Dark green
μ (cm^{-1})	15.22	16.52
Crystal size (mm^3)	0.80 × 0.25 × 0.10	0.10 × 0.25 × 0.40
Collection method	$\omega - 2\theta$	$\omega - 2\theta$
$\Delta\omega$ (°)	0.60 + 0.35 tgθ	0.60 + 0.35 tgθ
2θ range (°)	2, 54	2, 50
Data collected	3491	4373
Unique data	3301	4108
Data used [$I > 3\sigma(I)$]	2938	3019
Variables	322	313
R, R_w	0.051, 0.067	0.054, 0.064
Goodness of fit	1.86	1.48
$(\Delta/\sigma)_{max}$	0.02	0.06
$\Delta\rho_{max}$ (e Å^{-3})	1.44	1.13
$\Delta\rho_{min}$ (e Å^{-3})	−0.75	−0.92

RESULTS AND DISCUSSION

Spectroscopic properties

The representative IR spectra are shown in Fig. 1. The spectra of the complexes resemble those of pure hemicyanines and $[NBu_4]_2[Mo_6O_{19}]$. The IR spectra of the polyoxoanion in the three complexes are very similar ; four IR bonds (cm^{-1}) can be identified, i.e. 960, 800, 598 and 442. Mixing yellow solutions of hexamolybdate and red or dark red hemicyanines gave dark green microcrystalline solids. This suggests that an electronic interaction between the inorganic acceptor and the organic donor has occurred, which is able to induce sizeable red shifts in the charge-transfer absorption spectrum of the polyoxoanion.

Figure 2 compares the diffuse reflectance electronic spectra of the three complexes with hemicyanine dyes and the tetrabutylammonium salt of hexamolybdate, respectively. It is interesting that hemicyanine dyes induce large shifts of the low-energy tail of the charge-transfer absorption band from 516 nm for 2-DAPPI to 566 nm for complex **1**, from 598 nm for 4-DAPP to 630 nm for complex **2**, and from 658 nm for 4-DAPQ to 692 nm for complex **3**. The main outcome of these spectra is that the charge-transfer interaction, responsible for the red shift of the band tail, is essentially a solid-state effect.[5] Accordingly, Marder *et al.* expected the hyperpolarizability (β) to increase with increasing donor and acceptor strength.[13] Then, increasing λ_{max} by the charge transfer could be favourable to the non-linear optical, and photorefractive properties and for optical storage materials.[14–16]

Structural studies

Crystal structure of complex **1**. The crystal structure unit cell of complex is shown in Fig. 3. The 2-

Table 2. Bond distances (Å) of complex **1**

Mo(1)—O(1)	1.666(5)	N(01)—C(03)	1.44(1)
Mo(1)—O(12)	1.898(5)	N(1)—C(3)	1.354(9)
Mo(1)—O(13)	1.919(5)	N(1)—C(2)	1.44(1)
Mo(1)—O(31)	1.919(4)	N(1)—C(1)	1.47(1)
Mo(1)—O(21)	1.954(5)	N(2)—C(12)	1.348(8)
Mo(1)—O(123)	2.317(2)	N(2)—C(11)	1.376(8)
Mo(2)—O(2)	1.677(5)	N(2)—C(16)	1.483(9)
Mo(2)—O(32)	1.896(5)	C(3)—C(8)	1.40(1)
Mo(2)—O(21)	1.903(5)	C(3)—C(4)	1.42(1)
Mo(2)—O(12)	1.953(5)	C(4)—C(5)	1.36(1)
Mo(2)—O(23)	1.973(5)	C(5)—C(6)	1.41(1)
Mo(2)—O(123)	2.319(1)	C(6)—C(7)	1.41(1)
Mo(3)—O(3)	1.678(5)	C(6)—C(9)	1.43(1)
Mo(3)—O(23)	1.891(5)	C(7)—C(8)	1.37(1)
Mo(3)—O(13)	1.919(5)	C(9)—C(10)	1.35(1)
Mo(3)—O(31)	1.923(5)	C(10)—C(11)	1.438(9)
Mo(3)—O(32)	1.961(5)	C(11)—C(15)	1.41(1)
Mo(3)—O(123)	2.3205(8)	C(12)—C(13)	1.35(1)
O(01)—C(01)	1.21(1)	C(13)—C(14)	1.38(1)
N(01)—C(01)	1.32(1)	C(14)—C(15)	1.36(1)
N(01)—C(02)	1.44(1)		

DAPP cation is planar with a dihedral angle of 1.89° for the two aromatic rings. The bond lengths of C(9)—C(10), C(6)—C(9) and C(10)—C(11) are 1.35(1), 1.43(1) and 1.438(9) Å, respectively, which indicates that the cation possesses a conjugate configuration which is favourable to the polarization according to the idea of Marder *et al.* about the correlation between the bond length alternation (BLA) and hyperpolarizabilites β.[17,18] The BLA (−0.09) of complex **1** is higher than that of 1-methyl-4-(2-(4-hydroxyphenyl)vinyl)pyridinium 4-toluenesulphonate (−0.17)[19] and the complex of [2-DAPP][Ni(PDDT)] (−0.13),[20] which is due to the effect of the different anion. According to Marder's diagram of β *vs* BLA,[17] the β of complex **1** is obtained as approximately 60×10^{-30} esu, indicating that charge transfer of hemicyanine can be induced by the polyoxoanion and the electron-acceptor ability of polyoxoanion is stronger than that of 4-toluenesulphonate and Ni(PDDT)$^-$. The average Mo—O bond distances in $[Mo_6O_{19}]^{-2}$ are very similar to those reported previously,[21,22] i.e. 1.674(5) Å for Mo—O_t(terminal), 1.925(5) Å for Mo—O_b (bridging) and 2.318(5) Å for Mo—O_c (central). The crystal structure consists of one-dimensional staggering DADA stacks of 2-DAPP along the *c* axis. The plane of Mo(3)—Mo(2)—Mo(3)—Mo(2) in the hexamolybdate anion is orientated at 63.57° to the 2-DAPP and fits into channels formed by 2-DAPP. The distance between O(32) of polyoxoanion and N(2) of pyridinium is 3.02 Å.

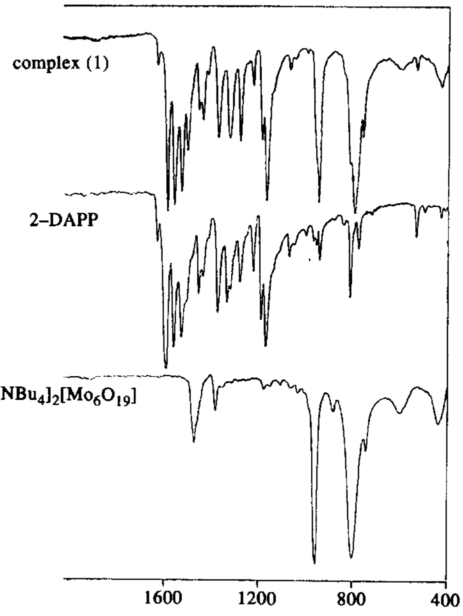


Fig. 1. IR spectrum of complex (**1**), 2-DAPP and $[NBu_4]_2[Mo_6O_{19}]$.

Crystal structure of complex **3**. The crystal structure of complex **3** and the stereoview of the molecular packing are shown in Fig. 4. The cation of [4-(2-dimethylaminophenyl)ethenyl]quinolinium (DAPQ) is also a planar conjugated structure. The bond lengths of C(9)—C(10), C(6)—C(9) and C(10)—C(11) are 1.34(1), 1.43(1) and 1.46(1) Å, respectively. The BLA (−0.10) of complex **3** is

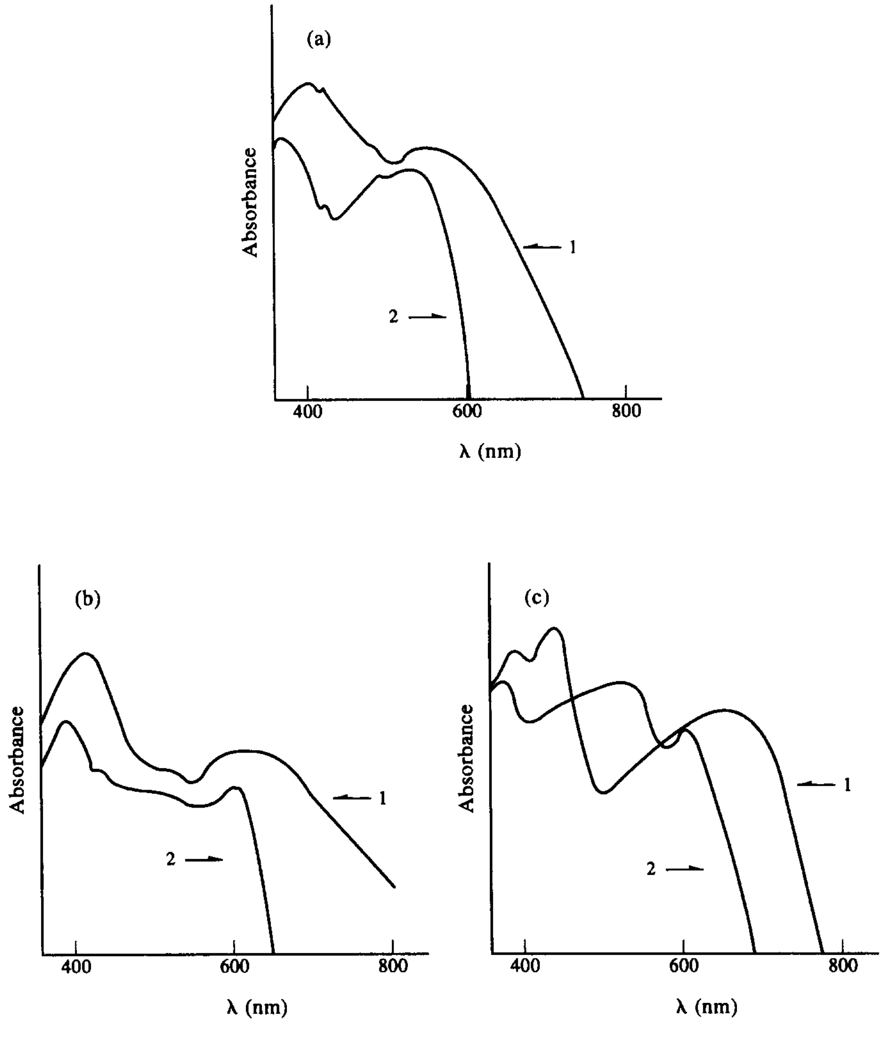


Fig. 2. The diffuse-reflectance electronic spectrum: (a) 1 for complex **1**, 2 for 2-DAPP; (b) 1 for complex **2**, 2 for 4-DAPP; (c) 1 for complex **3**, 2 for 4-DAPQ, in the region 800–350 nm.

Table 3. Bond angles (°) of complex **1**

O(1)—Mo(1)—O(12)	104.0(2)	O(21)—Mo(2)—O(123)	77.5(1)
O(1)—Mo(1)—O(13)	105.1(2)	O(12)—Mo(2)—O(23)	84.2(2)
O(1)—Mo(1)—O(31)	102.2(2)	O(12)—Mo(2)—O(123)	75.9(1)
O(1)—Mo(1)—O(21)	102.4(2)	O(23)—Mo(2)—O(123)	76.4(1)
O(1)—Mo(1)—O(123)	178.1(2)	O(3)—Mo(3)—O(23)	104.0(3)
O(12)—Mo(1)—O(13)	88.7(2)	O(3)—Mo(3)—O(13)	103.7(3)
O(12)—Mo(1)—O(31)	87.1(2)	O(3)—Mo(3)—O(31)	103.7(2)
O(12)—Mo(1)—O(21)	153.5(2)	O(3)—Mo(3)—O(32)	102.3(2)
O(12)—Mo(1)—O(123)	76.9(1)	O(3)—Mo(3)—O(123)	178.2(2)
O(13)—Mo(1)—O(31)	152.7(2)	O(23)—Mo(3)—O(13)	88.5(2)
O(13)—Mo(1)—O(21)	85.9(2)	O(23)—Mo(3)—O(31)	89.3(2)
O(13)—Mo(1)—O(123)	76.5(1)	O(23)—Mo(3)—O(32)	153.7(2)
O(31)—Mo(1)—O(21)	85.9(2)	O(23)—Mo(3)—O(123)	77.9(1)
O(31)—Mo(1)—O(123)	76.2(1)	O(13)—Mo(3)—O(31)	152.2(2)
O(21)—Mo(1)—O(123)	76.6(1)	O(13)—Mo(3)—O(32)	84.6(2)
O(2)—Mo(2)—O(32)	102.4(2)	O(13)—Mo(3)—O(123)	76.4(1)
O(2)—Mo(2)—O(21)	103.1(2)	O(31)—Mo(3)—O(32)	85.3(2)
O(2)—Mo(2)—O(12)	103.6(2)	O(31)—Mo(3)—O(123)	76.1(1)
O(2)—Mo(2)—O(23)	104.0(2)	O(32)—Mo(3)—O(123)	75.9(1)
O(2)—Mo(2)—O(123)	179.3(2)	Mo(1)—O(123)—Mo(1)	180.00
O(32)—Mo(2)—O(21)	89.4(2)	Mo(1)—O(123)—Mo(2)	90.20(5)
O(32)—Mo(2)—O(12)	87.0(2)	Mo(1)—O(123)—Mo(2)	89.80(5)
O(32)—Mo(2)—O(23)	153.4(2)	Mo(1)—O(123)—Mo(3)	89.82(4)
O(32)—Mo(2)—O(123)	77.1(1)	Mo(1)—O(123)—Mo(3)	90.18(4)
O(21)—Mo(2)—O(12)	153.3(2)	Mo(1)—O(123)—Mo(2)	89.80(5)
O(21)—Mo(2)—O(23)	87.3(2)	Mo(1)—O(123)—Mo(2)	90.20(5)
Mo(1)—O(123)—Mo(3)	90.18(4)	C(8)—C(3)—C(4)	116.4(6)
Mo(1)—O(123)—Mo(3)	89.82(4)	C(5)—C(4)—C(3)	121.5(7)
Mo(2)—O(123)—Mo(2)	180.00	C(4)—C(5)—C(6)	122.0(6)
Mo(2)—O(123)—Mo(3)	89.83(3)	C(5)—C(6)—C(7)	116.4(6)
Mo(2)—O(123)—Mo(3)	90.17(3)	C(5)—C(6)—C(9)	124.0(6)
Mo(2)—O(123)—Mo(3)	90.17(3)	C(7)—C(6)—C(9)	119.6(6)
Mo(2)—O(123)—Mo(3)	89.83(3)	C(8)—C(7)—C(6)	121.4(7)
Mo(3)—O(123)—Mo(3)	180.00	C(7)—C(8)—C(3)	122.4(6)
Mo(1)—O(12)—Mo(3)	117.0(2)	C(10)—C(9)—C(6)	127.5(7)
Mo(1)—O(13)—Mo(3)	117.1(2)	C(9)—C(10)—C(11)	122.3(6)
Mo(2)—O(21)—Mo(1)	116.0(2)	N(2)—C(11)—C(15)	115.8(6)
Mo(3)—O(23)—Mo(2)	115.9(2)	N(2)—C(11)—C(10)	119.6(6)
Mo(1)—O(31)—Mo(3)	117.5(2)	C(15)—C(11)—C(10)	124.7(6)
Mo(2)—O(32)—Mo(3)	116.8(2)	N(2)—C(12)—C(13)	122.5(6)
C(01)—N(01)—C(02)	121.2(8)	C(12)—C(13)—C(14)	118.1(6)
C(01)—N(01)—C(03)	121.6(7)	C(15)—C(14)—C(13)	120.0(7)
C(02)—N(01)—C(03)	117.2(8)	C(14)—C(15)—C(11)	121.9(6)
O(01)—C(01)—N(01)	125.9(8)		
C(3)—N(1)—C(2)	122.1(7)		
C(3)—N(1)—C(1)	119.4(7)		
C(2)—N(1)—C(1)	118.0(6)		
C(12)—N(2)—C(11)	121.7(6)		
C(12)—N(2)—C(16)	117.8(6)		
C(11)—N(2)—C(16)	120.4(5)		
N(1)—C(3)—C(8)	123.0(7)		
N(1)—C(3)—C(4)	120.5(7)		

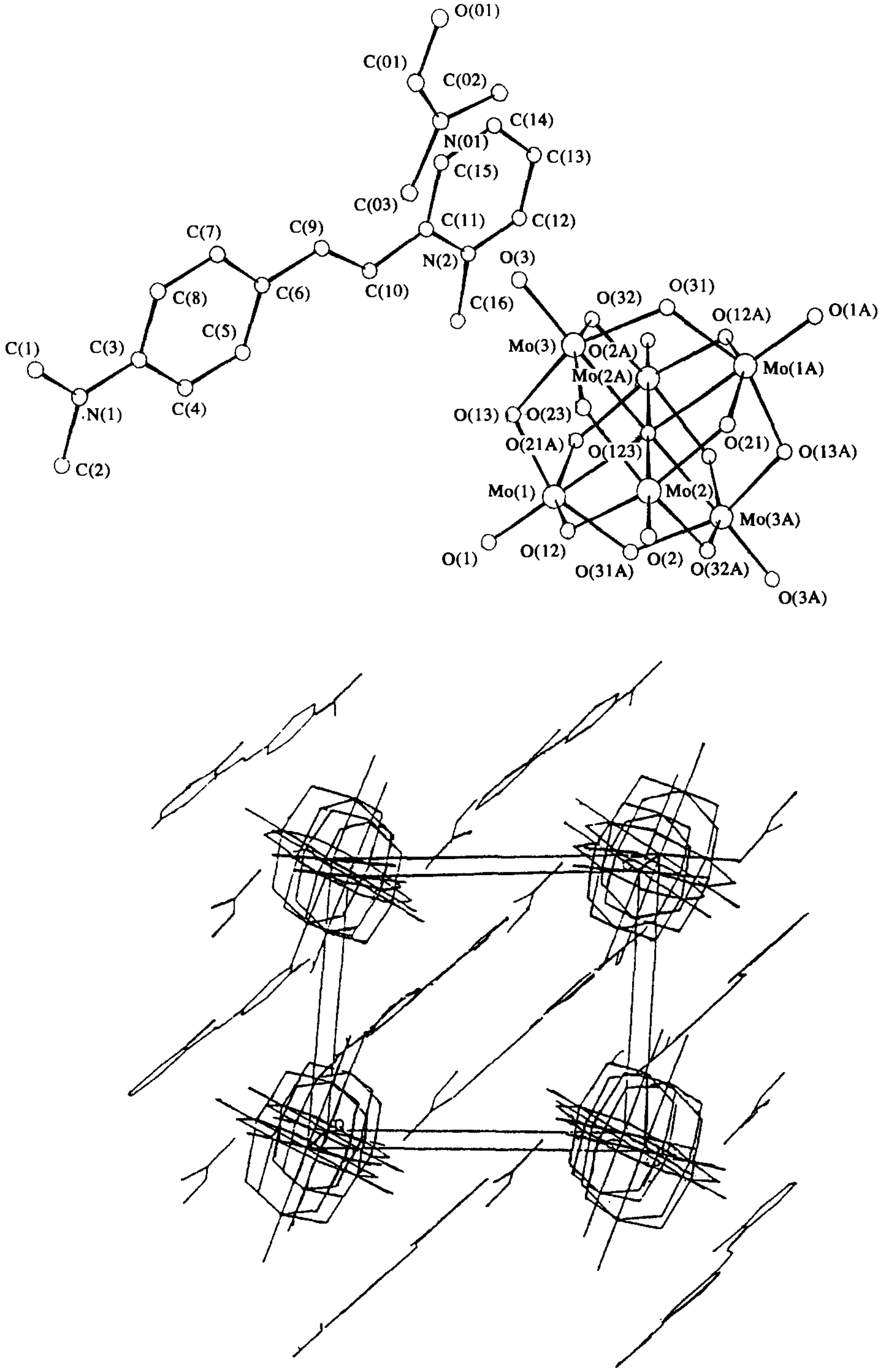


Fig. 3. The molecular structure and unit cell of complex 1.

Table 4. Bond distances (Å) of complex **3**

Mo(1)—O(1)	1.678(7)	N(2)—C(13)	1.31(1)
Mo(1)—O(31)	1.890(7)	N(2)—C(19)	1.40(1)
Mo(1)—O(12)	1.924(7)	N(2)—C(20)	1.46(1)
Mo(1)—O(13)	1.927(7)	C(3)—C(8)	1.42(1)
Mo(1)—O(21)	1.946(7)	C(3)—C(4)	1.43(1)
Mo(1)—O(123)	2.304(1)	C(4)—C(5)	1.36(1)
Mo(2)—O(2)	1.672(7)	C(5)—C(6)	1.40(1)
Mo(2)—O(32)	1.901(7)	C(6)—C(7)	1.42(1)
Mo(2)—O(21)	1.902(7)	C(6)—C(9)	1.43(1)
Mo(2)—O(12)	1.924(7)	C(7)—C(8)	1.36(1)
Mo(2)—O(23)	1.953(7)	C(9)—C(10)	1.34(1)
Mo(2)—O(123)	2.318(1)	C(10)—C(11)	1.46(1)
Mo(3)—O(3)	1.660(7)	C(11)—C(12)	1.38(1)
Mo(3)—O(23)	1.895(7)	C(11)—C(18)	1.44(1)
Mo(3)—O(13)	1.903(7)	C(12)—C(13)	1.39(1)
Mo(3)—O(31)	1.950(7)	C(19)—C(18)	1.40(1)
Mo(3)—O(32)	1.958(7)	C(19)—C(14)	1.41(2)
Mo(3)—O(123)	2.318(1)	C(18)—C(17)	1.39(1)
N(1)—C(3)	1.35(1)	C(17)—C(16)	1.35(2)
N(1)—C(1)	1.42(1)	C(16)—C(15)	1.40(2)
N(1)—C(2)	1.46(1)	C(15)—C(14)	1.35(2)

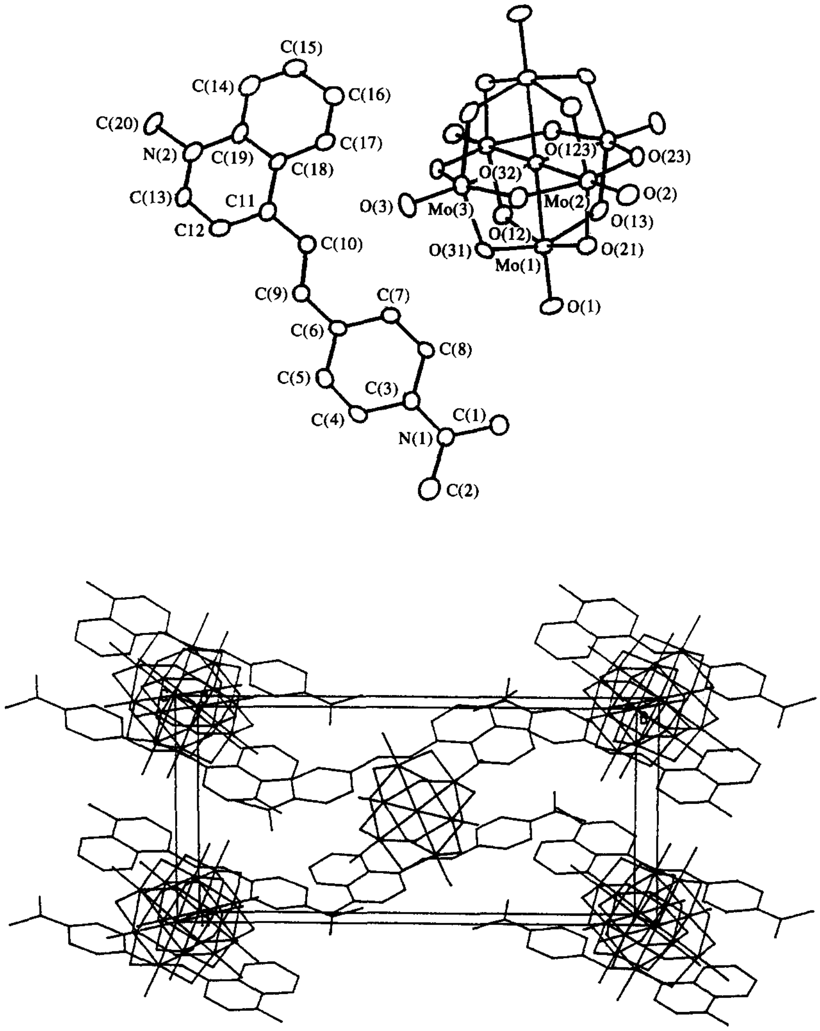


Fig. 4. The molecular structure and unit cell of complex 3.

Table 5. Bond angles (°) of complex **3**

O(1)—Mo(1)—O(31)	103.0(3)
O(1)—Mo(1)—O(12)	104.2(3)
O(1)—Mo(1)—O(13)	103.2(4)
O(1)—Mo(1)—O(21)	102.1(3)
O(1)—Mo(1)—O(123)	178.7(2)
O(31)—Mo(1)—O(12)	87.4(3)
O(31)—Mo(1)—O(13)	153.7(3)
O(31)—Mo(1)—O(21)	89.2(3)
O(31)—Mo(1)—O(123)	77.5(2)
O(12)—Mo(1)—O(13)	86.2(3)
O(12)—Mo(1)—O(21)	153.5(3)
O(12)—Mo(1)—O(123)	77.0(2)
O(13)—Mo(1)—O(21)	85.3(3)
O(13)—Mo(1)—O(123)	76.2(2)
O(21)—Mo(1)—O(123)	76.7(2)
O(2)—Mo(2)—O(32)	103.1(3)
O(2)—Mo(2)—O(21)	102.2(3)
O(2)—Mo(2)—O(12)	104.1(3)
O(2)—Mo(2)—O(23)	103.6(3)
O(2)—Mo(2)—O(123)	179.3(3)
O(32)—Mo(2)—O(21)	87.9(3)
O(32)—Mo(2)—O(12)	88.6(3)
O(32)—Mo(2)—O(23)	153.3(3)
O(32)—Mo(2)—O(123)	76.8(2)
O(21)—Mo(2)—O(12)	153.6(3)
O(21)—Mo(2)—O(23)	86.2(3)
Mo(1)—O(123)—Mo(3)	90.12(5)
Mo(1)—O(123)—Mo(3)	89.88(5)
Mo(2)—O(123)—Mo(2)	180.00
Mo(2)—O(123)—Mo(3)	90.40(5)
Mo(2)—O(123)—Mo(3)	89.60(5)
Mo(2)—O(123)—Mo(3)	89.60(5)
Mo(2)—O(123)—Mo(3)	90.40(5)
Mo(3)—O(123)—Mo(3)	180.00
Mo(3)—O(23)—Mo(2)	116.2(3)
Mo(3)—O(13)—Mo(1)	117.4(3)
Mo(1)—O(31)—Mo(3)	116.5(3)
Mo(2)—O(21)—Mo(1)	116.2(3)
Mo(2)—O(32)—Mo(3)	117.0(3)
Mo(1)—O(12)—Mo(2)	116.4(3)
C(3)—N(1)—C(1)	121(1)
C(3)—N(1)—C(2)	121.6(8)
C(1)—N(1)—C(2)	117.2(9)
C(13)—N(2)—C(19)	119.7(9)
C(13)—N(2)—C(20)	120(1)
C(19)—N(2)—C(20)	121(1)
N(1)—C(3)—C(8)	122.0(9)
N(1)—C(3)—C(4)	121(1)
C(8)—C(3)—C(4)	117(1)
C(5)—C(4)—C(3)	120(1)
C(4)—C(5)—C(6)	123(1)
C(5)—C(6)—C(7)	116(1)
O(21)—Mo(2)—O(123)	77.1(2)
O(12)—Mo(2)—O(23)	85.4(3)
O(12)—Mo(2)—O(123)	76.6(2)
O(23)—Mo(2)—O(123)	76.5(2)
O(3)—Mo(3)—O(23)	103.4(3)
O(3)—Mo(3)—O(13)	106.3(3)
O(3)—Mo(3)—O(31)	101.3(3)
O(3)—Mo(3)—O(32)	103.0(3)
O(3)—Mo(3)—O(123)	177.2(3)
O(23)—Mo(3)—O(13)	89.6(3)
O(23)—Mo(3)—O(31)	86.3(3)
O(23)—Mo(3)—O(32)	153.2(3)
O(23)—Mo(3)—O(123)	77.6(2)
O(13)—Mo(3)—O(31)	152.3(3)
O(13)—Mo(3)—O(32)	87.1(3)
O(13)—Mo(3)—O(123)	76.3(2)
O(31)—Mo(3)—O(32)	84.5(3)
O(31)—Mo(3)—O(123)	76.1(2)
O(32)—Mo(3)—O(123)	75.8(2)
Mo(1)—O(123)—Mo(1)	180.00
Mo(1)—O(123)—Mo(2)	89.92(5)
Mo(1)—O(123)—Mo(2)	90.08(5)
Mo(1)—O(123)—Mo(3)	89.88(5)
Mo(1)—O(123)—Mo(3)	90.12(5)
Mo(1)—O(123)—Mo(2)	90.08(5)
Mo(1)—O(123)—Mo(2)	89.92(5)
C(5)—C(6)—C(9)	120.3(9)
C(7)—C(6)—C(9)	123.9(9)
C(8)—C(7)—C(6)	122(1)
C(7)—C(8)—C(3)	121.2(9)
C(10)—C(9)—C(6)	128(1)
C(9)—C(10)—C(11)	125(1)
C(12)—C(11)—C(18)	118(1)
C(12)—C(11)—C(10)	121(1)
C(18)—C(11)—C(10)	121.3(9)
C(11)—C(12)—C(13)	121(1)
N(2)—C(13)—C(12)	123(1)
N(2)—C(19)—C(18)	120(1)
N(2)—C(19)—C(14)	120(1)
C(18)—C(19)—C(14)	119(1)
C(17)—C(18)—C(19)	118(1)
C(17)—C(18)—C(11)	122(1)
C(19)—C(18)—C(11)	119(1)
C(16)—C(17)—C(18)	122(1)
C(17)—C(16)—C(15)	119(1)
C(14)—C(15)—C(16)	121(1)
C(15)—C(14)—C(19)	120(1)

slightly lower than that of complex **1**, and its β is about 35×10^{-30}, this indicates again that polyoxoanion can induce charge transfer, which is consistent with the result of UV-vis spectra of this series of compounds. The average Mo—O bond distances are very similar to those found for complex **1**. In the unit cell, the DAPQ cations form a pair of one-dimensional stacked units. Like complex **1** the plane containing Mo(3)—Mo(2)—Mo(3′)—Mo(2′) in $Mo_6O_{19}^{2-}$ is orientated to 4-DAPP at 61.21° and fits into the channels formed by DAPQ. The polyoxoanion is close to the quinolinium moiety with a [O(1) ··· N(2)] distance of 3.00 Å

This DAPQ compound crystallized in a centrosymmetric arrangement ($P2_1/n$) and features a head-to-tail pairing of the cations, and formed a pairing DADA-type stack with a distance of 3.45 Å between the pairs. (In complex **1** this distance is about 3.56 Å.) This excellent alignment of chromophores within a given row is favourable to a π-stack.[9]

A series of charge-transfer salts derived from hemicyanine dyes and hexamolybdate have been reported. It is possible to use this kind of compound *via* organic salt methodology[9] to obtain potential materials with large χ^2 Testing of these complexes revealed an absence of SHG due to the centrosymmetry.

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