Organic–Inorganic Charge-transfer Salts based on the β-$[Mo_8O_{26}]^{4-}$ Isopolyanion: Synthesis, Properties and X-Ray Structure*

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The complex reaction between the organic electron donor *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (tmpd) and the inorganic acceptor $[Mo_6O_{19}]^{2-}$ in air has been investigated. Conversion of the inorganic polyanion to β-$[Mo_8O_{26}]^{4-}$, as well as protonation and/or oxidation of the organic base are possible. Different charge-transfer salts of the type β-$[Htmpd]_x[tmpd]_{4-x}[Mo_8O_{26}]$ and β-$[Htmpd]_x[tmpd]_{3-x}[HMo_8O_{26}]$ have been isolated and characterized. They contain positively charged tetramethyl-*p*-phenylenediamine molecules which may be present, simultaneously or not, as monoprotonated units ($Htmpd^+$) or radical cations ($tmpd^+$). According to optical and magnetic properties, isolated radicals or tightly bound dimers have been found. The X-ray crystal and molecular structure of β-$[Htmpd]_2[tmpd]_2[Mo_8O_{26}]$ has been solved by the heavy-atom method and refined to a final $R = 0.057$ for 3129 reflections with $I \geqslant 3\sigma(I)$; monoclinic, space group $P2_1/c$ with $a = 11.607(5)$, $b = 24.830(9)$, $c = 11.047(4)$ Å, $\beta = 106.82(3)^\circ$ and $Z = 2$. The β-octamolybdate polyanion has the well known Lindqvist structure. The radical cations form eclipsed dimeric units with an intradimeric distance 3.35 Å and do not interact with the polyanion. The protonated molecules are isolated from one another, but linked to the polyanion through bifurcated hydrogen bonds of 2.87 and 3.11 Å.

Recent work has highlighted the ability of the well known early transition-metal polyoxoanions[1] to promote the stacking and electronic interaction of planar, conjugated organic molecules.[2] Several new charge-transfer salts, based upon these large, quasi-spherical, oxidic cluster anions, as inorganic acceptors and tetrathiafulvalene {[2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole]} or related molecules as organic donors are presently being reported in the literature.[3–7] Polyoxoanions are complex, chemically tunable redox systems and allow the isolation of a range of molecular solids with novel structural, magnetic and transport properties. In addition weak, direct electronic interaction between the organic donor and its inorganic counterpart is possible in many of these polyoxoanion-based charge-transfer salts. Therefore modelling of the interaction between organic substrates and catalytic oxide surfaces and development of improved oxidation catalysts is also being pursued.[2,8–10]

The synthesis of truly reversible photochromic materials is another possible outcome of this work. Reversibility implies a simple photo-induced electron-transfer process not followed by major structural changes or further chemical evolution (*e.g.* oxidation or protonation) of either the donor or acceptor components of the photochromic molecule [equation (1)].

$$(\text{cation})_n^{n+}(\text{donor})(\text{polyoxoanion})^{n-} \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} (\text{cation})_n^{n+}(\text{donor}^+)(\text{polyoxoanion})^{(n+1)-} \qquad (1)$$

Many photochromic polyoxoanion salts have been reported in the literature,[11] however, they generally do not meet the above criteria leading to redox processes which are, on the whole, irreversible.

This paper reports the synthesis and structural and magnetic characterization of some charge-transfer salts formed by the β-octamolybdate anion and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine. Aromatic amines are known to undergo a series of photophysical and photochemical processes based on electron transfer.[12–14] The compounds reported below contain the diamine molecule both as a cationic ($tmpd^+$ radical cation) and donor (monoprotonated $Htmpd^+$) component and represent a preliminary step towards the above aim, provided that fine tuning of the redox potential can be achieved.

Experimental

Reagents.—All materials and organic solvents were reagent grade and used as supplied. The amine $C_6H_4(NMe_2)_2$-*p* was vacuum sublimed and stored under nitrogen. The compounds $[NBu_4]_2[Mo_6O_{19}]$, α-$[NBu_4]_4[Mo_8O_{26}]$ and $[tmpd]BPh_4$ were prepared and purified according to literature methods.[15,16] The reagent $[Htmpd]_2[BPh_4]_2$ was obtained by simple metathesis between *p*-$(Me_2N)_2C_6H_4{\cdot}2HCl$ and $NaBPh_4$ in water. Elemental analyses were performed either by the Servizio Microanalitico, Area della Ricerca di Roma, CNR (C, H, N) or by H. Malissa Analitische Laboratorien, Elbach, Germany (other elements).

Preparation of β-$[Htmpd]_2[tmpd]_2[Mo_8O_{26}]$ **1**.—Solid $C_6H_4(NMe_2)_2$-*p* (144 mg, 0.88 mmol) was added at room temperature to a solution of $[NBu_4]_2[Mo_6O_{19}]$ in MeCN (15 cm^3). After stirring for a few minutes and then filtering, the yellowish solution was set aside to evaporate. It slowly turned purple, depositing, after one night, well formed dark crystals of compound **1** and colourless or light blue aggregates (compound **2**). Slowing down the evaporation rate increased the amount of dark crystals eventually yielding pure compound **1**. IR spectroscopy clearly indicates that both compounds contain the β-$[Mo_8O_{26}]^{4-}$ anion. Their elemental analyses are closely similar and, according to spectroscopic and structural data, they are formulated as β-$[Htmpd]_2[tmpd]_2[Mo_8O_{26}]$ **1** (Found: C, 25.45; H, 3.55; Mo, 40.50; N, 5.75. Calc.: C, 26.0; H, 3.60; Mo, 41.65; N, 6.10%) and β-$[Htmpd]_4[Mo_8O_{26}]$ **2**

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

(Found: C, 26.15; H, 3.70; Mo, 41.45; N, 6.00. Calc.: C, 26.05; H, 3.70; Mo, 41.60; N, 6.10%).

Preparation of β-[Htmpd]$_2$[tmpd][HMo$_8$O$_{26}$] **3**.—The amine $C_6H_4(NMe_2)_2$-*p* (144 mg, 0.88 mmol) and [NBu$_4$]$_2$[Mo$_6$O$_{19}$] (300 mg, 0.22 mmol) were dissolved in MeCN (15 cm^3). The solution was heated to close to its boiling point and water (7.5 cm^3) was added dropwise with stirring. After heating for another few minutes the clear, dark blue solution was left to cool. After 12 h a homogeneous, crystalline, blue-purple precipitate (150 mg) was collected. Compound **3** contains the β-[Mo$_8$O$_{26}$]$^{4-}$ anion (IR spectroscopy) and analyses as β-[Htmpd]$_2$[tmpd][HMo$_8$O$_{26}$] (Found: C, 21.80; H, 3.50; Mo, 41.55; N, 5.00. Calc: C, 21.50; H, 2.95; Mo, 41.70; N, 5.00%).

Preparation of β-[tmpd]$_3$[HMo$_8$O$_{26}$] **4**.—The amine $C_6H_4(NMe_2)_2$-*p* (360 mg, 2.20 mmol) and α-[NBu$_4$]$_4$[Mo$_8$O$_{26}$] (945 mg, 0.44 mmol) were dissolved in MeCN (90 cm^3). The solution was irradiated at room temperature for 1 h in a Pyrex, water-cooled immersion reactor equipped with a 125 W Hg lamp. The reaction was run under a slight overpressure of oxygen. The solution rapidly turned blue and a dark microcrystalline precipitate was formed which contains the β-[Mo$_8$O$_{26}$]$^{4-}$ anion and analyses as β-[tmpd]$_3$[HMo$_8$O$_{26}$] **4** (Found: C, 21.60; H, 3.10; N, 5.05. Calc.: C, 21.60; H, 3.10; N, 5.00%). If the reaction is run under nitrogen a mixture of the unreacted starting compounds is recovered by partially evaporating the solution. Direct synthesis of a fully radical analogue of compound **1**, *i.e.* β-[tmpd]$_4$[Mo$_8$O$_{26}$], was attempted similarly, but without success.

Preparation of β-[Htmpd]$_3$ [HMo$_8$O$_{26}$] **5**.—This compound can be conveniently obtained by precipitating appropriately acidified solutions of [MoO$_4$]$^{2-}$ in water with *p*-(Me$_2$N)$_2$C$_6$H$_4$·2HCl. Hydrochloric acid (6 mol dm^{-3}, 3 cm^3) was slowly added to a solution of $Na_2MoO_4 \cdot 2H_2O$ (1.25 g, 5 mmol) in water (3 cm^3) at room temperature with stirring. After a few minutes a solution of *p*-(Me$_2$N)$_2$C$_6$H$_4$·2HCl (1.18 g, 5 mmol) in water (10 cm^3) was added giving an immediate precipitate which was filtered off, thoroughly washed with water and dried under vacuum. This white-cream powder contains the β-[Mo$_8$O$_{26}$]$^{4-}$ anion and analyses as β-[Htmpd]$_3$[HMo$_8$O$_{26}$]·2H$_2$O **5** (Found: C, 20.45; H, 3.10; Mo, 44.20; N, 4.65. Calc.: C, 21.00; H, 3.30; Mo, 44.70; N, 4.90%). Direct synthesis of the fully protonated analogue of compound **1** (*i.e.* compound **2**) was attempted without success.

Preparation of [Htmpd]$_2$[Mo$_6$O$_{19}$] **6** *and* [tmpd]$_2$[Mo$_6$O$_{19}$] **7**.—These two compounds have been prepared only for the purpose of comparison and have not been fully characterized. The first one was easily obtained by metathesis between [Htmpd]$_2$[BPh$_4$]$_2$ and [NBu$_4$]$_2$[Mo$_6$O$_{19}$] in MeCN. The second was obtained by closely following the procedure given above for compound **4**. The two compounds which are, respectively, yellow and purple, showed satisfactory analyses and IR spectra consistent with their formulation.

Physical Measurements.—Thermogravimetric and differential thermal analyses were carried out under dry nitrogen on a Stanton-Redcroft STA-781 thermoanalyser. IR and optical spectra were recorded, respectively, on a Perkin-Elmer 983-G and a Cary 5 spectrophotometer. ESR spectra were obtained with a Varian E-9 X-band spectrometer equipped with a Bruker BNM-20 gaussmeter and a Systron-Donner 6246-A frequency counter. Magnetic susceptibility measurements were carried out on a commercial SQUID magnetometer (Quantum Design, $B_{max} \approx 5$ T).

Crystal Structure Determination of Complex **1**.—*Crystal data.* $C_{40}H_{66}Mo_8N_8O_{26}$, $M = 1842.52$, monoclinic, space group $P2_1/c$, $a = 11.607(5)$, $b = 24.830(9)$, $c = 11.047(4)$ Å, $\beta = 106.82(3)°$, $U = 3048(2)$ Å^3, $Z = 2$, $D_c = 2.009$ g cm^{-3}, $F(000) = 1812$, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 16.0 cm^{-1}.

A prismatic crystal (dimensions 0.2 × 0.2 × 0.6 mm) was used for the data collection on a Nicolet-automated four-circle diffractometer at room temperature, by the θ–2θ scan technique with graphite-monochromated Mo-Kα radiation. A total of 8080 independent reflections were collected, of which 3129 with $I > 3\sigma(I)$ were used in the refinement. They were corrected for Lorentz-polarization factors: there was no absorption correction. The structure was solved by Patterson and Fourier methods. Positional and anisotropic thermal parameters for non-hydrogen atoms were refined by full-matrix least squares, with the weighting scheme $w = 1/\sigma^2(F_0)$. Hydrogen atoms were introduced in calculated positions with one overall fixed isotropic thermal parameter $U = 0.25$ Å^2. Refinement converged to $R = 0.057$ ($R' = 0.053$). Neutral scattering factors (f' and f'' values) were used.[17] Computations were performed on a DG Eclipse/8000 II computer by using the SHELX 76 system of crystallographic programs.[18] Atomic coordinates are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Synthesis.—The organic base interacts with the [Mo$_6$O$_{19}$]$^{2-}$ anion in organic solvents or aqueous–organic mixtures to give a quite complicated sequence of reactions which may involve protonation and/or oxidation of the organic base as well as conversion or isomerization of the inorganic polyanion. Therefore, depending on the detailed experimental conditions, different final products may be isolated.

The simple reaction between the organic base and [Mo$_6$O$_{19}$]$^{2-}$ in reagent grade MeCN in air reproducibly affords dark blue crystals of complex **1**. The reaction involves both the known conversion reaction[19] of [Mo$_6$O$_{19}$]$^{2-}$ to β-[Mo$_8$O$_{26}$]$^{4-}$ as well as protonation and partial air oxidation of the base according to the following overall reaction scheme [equations (2)–(5)], where tmpd^0 is the neutral molecule.

$$4\,[\mathrm{Mo_6O_{19}}]^{2-} + 2\,\mathrm{H_2O} \longrightarrow 3\,\beta\text{-}[\mathrm{Mo_8O_{26}}]^{4-} + 4\,\mathrm{H}^+ \qquad (2)$$

$$6\,\mathrm{tmpd}^0 + 1.5\,\mathrm{O_2} + 3\,\mathrm{H_2O} \longrightarrow 6\,\mathrm{tmpd}^+ + 6\,\mathrm{OH}^- \qquad (3)$$

$$6\,\mathrm{tmpd}^0 + 6\,\mathrm{H_2O} \longrightarrow 6\,\mathrm{Htmpd}^+ + 6\,\mathrm{OH}^- \qquad (4)$$

$$4\,[\mathrm{Mo_6O_{19}}]^{2-} + 12\,\mathrm{tmpd}^0 + 1.5\,\mathrm{O_2} + 7\,\mathrm{H_2O} \longrightarrow 3\,\beta\text{-}[\mathrm{Htmpd}]_2[\mathrm{tmpd}]_2[\mathrm{Mo_8O_{26}}] + 8\,\mathrm{OH}^- \qquad (5)$$

It may be noted that complex **1**, as well as all the other compounds reported in this work, contains the β form of the octamolybdate anion whose presence is easily detected by IR spectroscopy. If evaporation of the above reaction solution is not slow enough variable amounts of feather-like, light blue, quasi-colourless crystals may be obtained (compound **2**). This latter salt shows elemental analyses and an IR spectrum almost identical to those of compound **1**, but is fully diamagnetic and has no optical spectrum. It has been later identified as β-[Htmpd]$_4$[Mo$_8$O$_{26}$].

Reaction between the organic base and [Mo$_6$O$_{19}$]$^{2-}$ has also been carried out in the presence of substantial amounts of water. In this case a blue-purple microcrystalline precipitate was obtained which turned out to be the monoprotonated salt β-[Htmpd]$_2$[tmpd][HMo$_8$O$_{26}$]. Compounds **4**–**7** have been synthesised by metathesis or photochemically essentially to support identification of the charge-transfer salts **1**–**3**.

Table 1 Atomic coordinates of the non-hydrogen atoms of compound **1**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	−0.047 7(1)	0.115 5(1)	−0.216 5(1)	C(1)	0.454(2)	0.051 2(8)	0.344(2)
Mo(2)	−0.208 5(1)	0.065 28(4)	−0.047 5(1)	C(2)	0.366(2)	0.056 3(9)	0.413(2)
Mo(3)	0.026 5(1)	0.021 35(4)	0.160 1(1)	C(3)	0.414(2)	0.075(1)	0.539(2)
Mo(4)	0.188 8(1)	0.071 23(4)	−0.001 0(1)	C(4)	0.532(2)	0.086(1)	0.589(2)
O(1)	−0.074 8(8)	0.134 9(4)	−0.367 5(9)	C(5)	0.617(2)	0.077 1(9)	0.515(2)
O(2)	−0.357 5(7)	0.052 2(3)	−0.082 9(8)	C(6)	0.574(2)	0.058 8(8)	0.396(2)
O(3)	0.052 0(7)	−0.026 8(3)	0.278 0(6)	C(7)	0.602(2)	0.028(1)	0.197(2)
O(4)	0.333 7(7)	0.064 0(3)	0.001 3(8)	C(8)	0.773(2)	0.072(2)	0.365(2)
O(5)	−0.010 1(5)	0.053 0(2)	−0.029 9(6)	C(9)	0.211(4)	0.075(2)	0.562(3)
O(11)	−0.035 2(8)	0.172 6(4)	−0.130 1(9)	C(10)	0.370(2)	0.119(2)	0.718(3)
O(12)	−0.200 6(6)	0.091 8(3)	−0.203 7(7)	C(11)	0.228(2)	0.265 9(9)	0.370(2)
O(14)	0.120 6(7)	0.095 8(3)	−0.166 2(7)	C(12)	0.342(2)	0.282 0(9)	0.454(2)
O(21)	−0.186 0(7)	0.121 3(3)	0.043 6(8)	C(13)	0.442(3)	0.254(1)	0.464(3)
O(23)	−0.146 3(6)	0.013 6(3)	0.095 5(6)	C(14)	0.416(3)	0.204(1)	0.408(3)
O(31)	0.037 3(7)	0.079 9(3)	0.238 2(7)	C(15)	0.300(3)	0.187(1)	0.331(2)
O(34)	0.183 4(5)	0.019 4(3)	0.132 2(6)	C(16)	0.212(2)	0.220 5(9)	0.309(2)
O(41)	0.186 0(7)	0.126 9(3)	0.085 6(7)	C(17)	−0.000(2)	0.196(1)	0.295(3)
N(1)	0.654(2)	0.049(1)	0.326(2)	C(18)	0.049(3)	0.240(1)	0.117(2)
N(2)	0.340(2)	0.081(2)	0.623(3)	C(19)	0.565(2)	0.323(1)	0.615(3)
N(3)	0.089(2)	0.202 5(8)	0.227(2)	C(20)	0.644(3)	0.239(2)	0.546(6)
N(4)	0.551(2)	0.270 4(9)	0.554(3)				

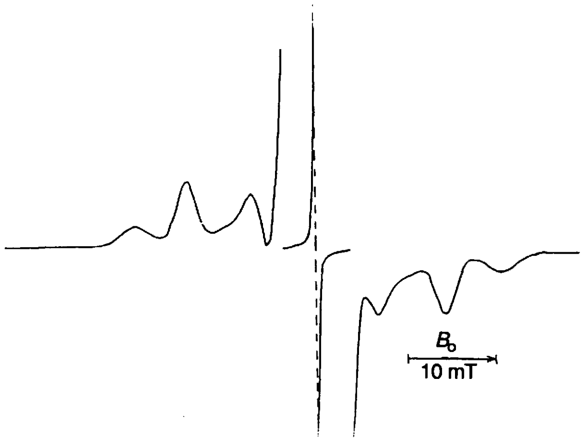

Fig. 1 Room-temperature, X-band ESR spectrum of polycrystalline β-$[Htmpd]_2[tmpd]_2[Mo_8O_{26}]$ showing the fine structure due to the rhombic $(tmpd^+)_2$ triplets

Spectroscopic and Magnetic Properties.—Compounds **1**–**3** exhibit closely similar, very rich IR spectra. The polyoxoanion region, below 1000 cm^{-1}, with bands at 950, 910, 850, 818, 718 and 653 cm^{-1} clearly shows that the starting $[Mo_6O_{19}]^{2-}$ anion has been converted to the β isomer of the octamolybdate anion.[19] Analysis of the vibrations due to the aromatic amine is less simple. However, the presence of N–H stretching and deformation vibrations indicates that in all compounds the amine is present, at least partly, as the protonated base. In addition compounds **1** and **3** exhibit characteristic shifts of some of the aromatic amine bands, *e.g.* those at 1323 and 1210 cm^{-1} previously assigned as ring-nitrogen vibrations,[20] supporting the simultaneous presence of the amine as protonated units and radical cations.

This finding is confirmed by the powder, room-temperature, electronic reflectance spectra of compounds **1** and **3** recorded in the visible and near-infrared regions. Compound **1** has bands centred at 26 700 (sh), 18 500, 16 400 (sh) and 13 000 cm^{-1}. The origin of these bands is well established[21] and they have been assigned as molecular excitations of monomeric tmpd$^+$ and intradimer charge-transfer transitions of the type $(tmpd^+)_2$ $(tmpd^0\text{–}tmpd^{2+})$, the low-energy band being diagnostic of the presence of dimeric tmpd$^+$. Compound **3** exhibits a substantially similar spectrum [absorption maxima at 26 700 (sh), 18 600 and 16 200 cm^{-1}] which, however, lacks the band at 13 000 cm^{-1}, thus suggesting that isolated tmpd$^+$ radical cations are present in this case.

Polycrystalline and solution ESR spectra of compounds **1** and **3** have been obtained at 300 and 77 K. A representative spectrum is shown in Fig. 1. At room temperature compound **1** shows a well resolved fine structure typical of a rhombic triplet. This spectrum does not show appreciable changes down to liquid nitrogen temperature, thus confirming that isolated, essentially non-interacting dimers are present. The measured magnetic parameters are $g = 2.0035$, $D = 198.2 \times 10^{-4}$ cm^{-1} and $E = 26.5 \times 10^{-4}$ cm^{-1}. In the case of compound **3** no fine structure has been detected down to 77 K. Room-temperature dilute solutions of compounds **1** and **3** in dimethylformamide, under an inert atmosphere, show the well known spectrum of the tmpd$^+$ radical cation.[22]

The bulk magnetic properties of compounds **1** and **3** are summarized in Figs. 2 and 3 where the corrected direct and inverse molar susceptibilities are given, as a function of temperature, together with the calculated best-fit curves.

For compound **3** the temperature dependence of the corrected susceptibility ($\chi_{dia} = -7.30 \times 10^{-4}$ cm^3 mol^{-1}) may be fitted to the Curie–Weiss expression (6). Best-fit parameters

$$\chi_{para} = C/(T - \theta) + N_\alpha \qquad (6)$$

are $C = 0.357$ cm^3 K mol^{-1}, $\theta \approx 0$ and N_α (temperature-independent paramagnetism) 1.84×10^{-3} cm^3 mol^{-1}. This latter value corresponds to a temperature-independent contribution of 2.30×10^{-4} cm^3 mol^{-1} per molybdenum atom, a value which, although higher, is essentially in agreement with other reported results.[23] The best-fit parameters show that compound **3** behaves as a simple doublet paramagnet ($\mu = 1.69$) and does not exhibit detectable magnetic interactions, thus suggesting that it contains isolated tmpd$^+$ radical cations.

As expected compound **1** exhibits a totally different behaviour and its experimental susceptibility can be interpreted as due to a strongly coupled dimer in the presence of a small monomeric, paramagnetic impurity. Low-temperature data have been fitted to expression (7), where the first term is the

$$\chi = p\, C/T + (1 - p)\, 1/T\,[1 + \tfrac{1}{3}\exp(-2J/KT)]^{\frac{1}{2}} + N_\alpha \qquad (7)$$

Curie susceptibility of the monomeric impurity and the second is the standard Van Vleck equation for the dimer,[23] assuming an interaction of the form $H = -2\, JS_1S_2$; p is the percentage of

Table 2 Bond lengths (Å) of compound **1** with e.s.d.s in parentheses

Mo(1)–O(1)	1.68(2)	Mo(3)–O(3)	1.728(8)	N(1)–C(6)	1.39(3)	N(3)–C(16)	1.52(4)
Mo(1)–O(5)	2.515(7)	Mo(3)–O(5)	2.165(7)	N(1)–C(7)	1.47(4)	N(3)–C(17)	1.46(4)
Mo(1)–O(11)	1.693(9)	Mo(3)–O(23)	1.934(7)	N(1)–C(8)	1.45(4)	N(3)–C(18)	1.49(4)
Mo(1)–O(12)	1.913(7)	Mo(3)–O(31)	1.675(8)	N(2)–C(3)	1.44(3)	N(4)–C(13)	1.42(5)
Mo(1)–O(14)	1.933(8)	Mo(3)–O(34)	1.934(6)	N(2)–C(9)	1.47(5)	N(4)–C(19)	1.47(4)
Mo(1)–O(3^I)	2.301(8)	Mo(3)–O(5^I)	2.314(6)	N(2)–C(10)	1.38(5)	N(4)–C(20)	1.36(5)
Mo(2)–O(2)	1.690(8)	Mo(4)–O(4)	1.685(8)	C(1)–C(2)	1.44(3)	C(11)–C(12)	1.43(4)
Mo(2)–O(5)	2.275(6)	Mo(4)–O(5)	2.283(6)	C(1)–C(6)	1.36(3)	C(11)–C(16)	1.30(3)
Mo(2)–O(12)	1.874(8)	Mo(4)–O(14)	1.870(9)	C(2)–C(3)	1.42(3)	C(12)–C(13)	1.33(4)
Mo(2)–O(21)	1.693(8)	Mo(4)–O(34)	1.969(7)	C(3)–C(4)	1.36(3)	C(13)–C(14)	1.37(4)
Mo(2)–O(23)	2.002(7)	Mo(4)–O(41)	1.687(7)	C(4)–C(5)	1.46(3)	C(14)–C(15)	1.43(5)
Mo(2)–O(34^I)	2.354(7)	Mo(4)–O(23^I)	2.339(7)	C(5)–C(6)	1.34(3)	C(15)–C(16)	1.30(4)

Symmetry code: I −*x*, −*y*, −*x*.

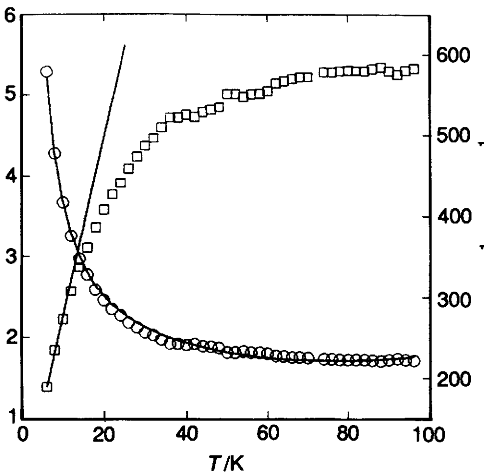

Fig. 2 Low-temperature direct (○) and inverse (□) magnetic susceptibility of β-[Htmpd]$_2$[tmpd]$_2$[Mo$_8$O$_{26}$] *versus* temperature. Full lines represent best-fit curves

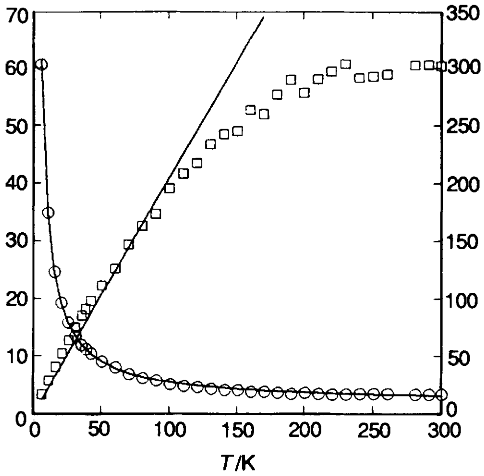

Fig. 3 Direct (○) and inverse (□) magnetic susceptibility of β-[Htmpd]$_2$[tmpd][HMo$_8$O$_{26}$] *versus* temperature. Full lines represent best-fit curves (see text)

the paramagnetic impurity. Best-fit values are $p = 5\%$, $C = 0.465$ cm^3 K mol^{-1} ($\mu = 1.93$), $2J = -340$ cm^{-1} and $N_\alpha = 1.34 \times 10^{-3}$ cm^3 mol^{-1}; J represents the isotropic part of the exchange interaction, whereas the very small anisotropic contribution can be obtained from the ESR results ($J_z = \frac{4}{3} D = 0.026$ cm^{-1}).

Crystal Structure of Compound **1**.—The crystal-structure analysis revealed the existence of β-[Mo$_8$O$_{26}$]$^{4-}$ anions and of two crystallographically independent cations, *i.e.* (Me$_2$N–C$_6$H$_4$–NMe$_2$)$^+$ (A) and (Me$_2$HN–C$_6$H$_4$–NMe$_2$)$^+$ (B), which are, respectively, the oxidized radical and the monoprotonated amine.

The structure of the β-octamolybdate polyanion, originally studied by Lindqvist,[24] consists of eight distorted MoO$_6$ octahedra sharing edges and corners and contains a centre of symmetry (see Fig. 4). In the present structure the distortion of the MoO$_6$ octahedra, deducible from the Mo–O bond lengths (Table 2) and O–Mo–O bond angles (Table 3), is comparable with that found in similar structures.[25] The three non-equivalent types of oxygens, *i.e.* the sixteen terminal (O$_t$), the eight bridging (O$_b$) and the central ones (O$_c$), form three families of Mo–O distances: the shortest are the Mo–O$_t$ with a mean value {e.s.d.s calculated as $[\Sigma_j(x_j - x)^2/n - 1]^{\frac{1}{2}}$} of 1.691(16) Å, with Mo–O$_b$ 1.929(44) Å and Mo–O$_c$ 2.318(98) Å. In Fig. 4 the shapes of the two types of cations are shown together with the proximities of cation B to the oxygen atoms O(31) and O(41) of the polyanion. The cations of type A, related to each other by centres of inversion at (½, 0, ½) and at (½, ½, 0) form dimer units in almost completely eclipsed conformations, with an intradimer distance of 3.35 Å (see Fig. 4). Such an interplanar spacing suggests a π-π interaction as found in other radical cations, *e.g.* tetrathiafulvalenium.[26] The planes of the methyl groups form small angles with respect to the phenylenediamine and, in particular, 9.5° for the plane containing the N(1), C(7) and C(8) atoms and 12.6° for the N(2), C(9) and C(10) atoms. There are no interactions, between the polyanion and cation A, the shortest contacts being those between O(12) and C(5) or C(4) of 3.24 and 3.28 Å respectively. In cation B only one of the two nitrogens, the N(4) atom bonded to C(19) and C(20) of the methyl group, is almost on the same plane as the phenylenediamine (the angle between the two planes being 5.5°). The other nitrogen N(3) actually forms a tetrahedral NMe$_2$ group, with a hydrogen atom in the fourth position clearly shown by a Fourier difference map. Such sp^3 hybridisation of the N(3) atom is also in accord with the N(3)–C(16) bond distance of 1.52(4) Å. This protonated cation is linked to the [Mo$_8$O$_{26}$]$^{4-}$ polyanion through bifurcated coplanar hydrogen bonds N(3)···O(41) 2.87 and N(3)···O(31) 3.11 Å. There are also interactions between C(17) and O(31), and between C(15) and O(41), of 3.02 and 3.04 Å, respectively. A view of the crystal packing is shown in Fig. 5.

Conclusion

The reaction between the inorganic acceptor [Mo$_6$O$_{19}$]$^{2-}$ and the organic electron donor *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine has been investigated. Two types of compounds, both containing the β-[Mo$_8$O$_{26}$]$^{4-}$ polyanion, and corresponding, respectively, to the neutral and acid charge-transfer salts of this polyanion with the organic base, have been isolated and characterised. These salts contain positively charged tetramethyl-*p*-phenylenediamine molecules, which may be present in the form of the monoprotonated base or the radical cation. Compounds **1** and **3** simultaneously contain

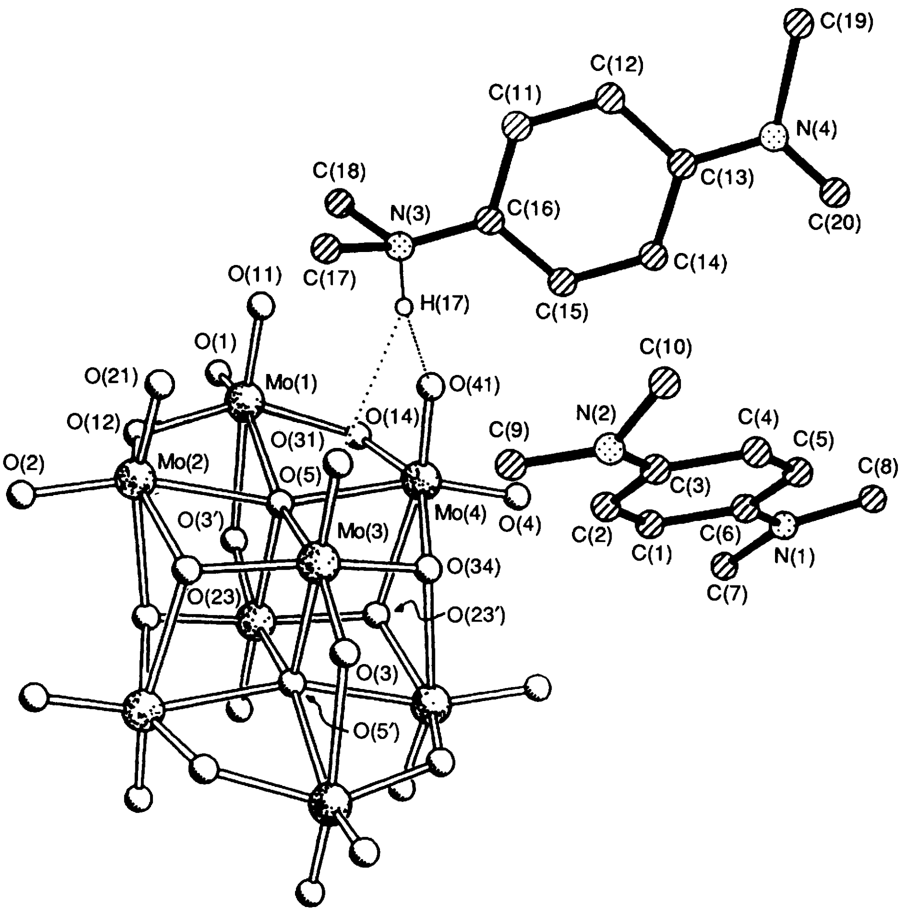

Fig. 4 Labelling scheme and perspective view of compound **1**, showing the hydrogen bonds. The hydrogen atoms of the methyl groups are omitted for clarity

Table 3 Bond angles (°) of compound **1** with e.s.d.s in parentheses

O(5)–Mo(1)–O(1)	158.6(3)	O(34^{I})–Mo(2)–O(23)	71.5(3)	O(23^{I})–Mo(4)–O(34)	72.4(3)	C(17)–N(3)–C(16)	114(2)
O(11)–Mo(1)–O(1)	106.3(5)	O(5)–Mo(3)–O(3)	157.5(3)	O(23^{I})–Mo(4)–O(41)	162.7(3)	C(18)–N(3)–C(16)	109(1)
O(12)–Mo(1)–O(1)	104.5(4)	O(23)–Mo(3)–O(3)	98.2(3)	Mo(1^{I})–O(3)–Mo(3)	117.1(4)	C(18)–N(3)–C(17)	112(2)
O(14)–Mo(1)–O(1)	104.0(4)	O(31)–Mo(3)–O(3)	103.9(4)	Mo(2)–O(5)–Mo(1)	85.2(2)	C(19)–N(4)–C(13)	123(2)
O(3^{I})–Mo(1)–O(1)	90.0(4)	O(34)–Mo(3)–O(3)	98.0(3)	Mo(3)–O(5)–Mo(1)	163.2(3)	C(20)–N(4)–C(13)	111(3)
O(11)–Mo(1)–O(5)	95.1(4)	O(5^{I})–Mo(3)–O(3)	83.3(3)	Mo(4)–O(5)–Mo(1)	85.4(2)	C(20)–N(4)–C(19)	124(3)
O(12)–Mo(1)–O(5)	72.2(3)	O(23)–Mo(3)–O(5)	77.7(3)	O(23)–O(5)–Mo(1)	133.4(3)	C(6)–C(1)–C(2)	124(2)
O(14)–Mo(1)–O(5)	71.8(3)	O(34)–Mo(3)–O(5)	77.5(3)	Mo(3^{I})–O(5)–Mo(1)	91.1(2)	C(3)–C(2)–C(1)	115(2)
O(3^{I})–Mo(1)–O(5)	68.6(2)	O(5^{I})–Mo(3)–O(5)	74.3(2)	Mo(3)–O(5)–Mo(2)	92.4(2)	C(2)–C(3)–N(2)	122(2)
O(3^{I})–Mo(1)–O(11)	163.7(4)	O(31)–Mo(3)–O(5)	98.6(3)	Mo(4)–O(5)–Mo(2)	160.6(3)	C(4)–C(3)–N(2)	116(2)
O(12)–Mo(1)–O(11)	98.4(4)	O(31)–Mo(3)–O(23)	101.1(4)	O(23)–O(5)–Mo(2)	48.2(2)	C(4)–C(3)–C(2)	122(1)
O(14)–Mo(1)–O(11)	97.8(4)	O(34)–Mo(3)–O(23)	149.6(3)	Mo(3^{I})–O(5)–Mo(2)	98.9(3)	C(5)–C(4)–C(3)	121(2)
O(14)–Mo(1)–O(12)	141.6(3)	O(5^{I})–Mo(3)–O(23)	78.5(3)	Mo(4)–O(5)–Mo(3)	91.7(3)	C(6)–C(5)–C(4)	119(2)
O(3^{I})–Mo(1)–O(12)	77.7(3)	O(34)–Mo(3)–O(31)	99.8(3)	O(23)–O(5)–Mo(3)	47.1(2)	C(1)–C(6)–N(1)	120(2)
O(3^{I})–Mo(1)–O(14)	77.1(3)	O(5^{I})–Mo(3)–O(31)	172.8(3)	Mo(3^{I})–O(5)–Mo(3)	105.7(3)	C(5)–C(6)–N(1)	119(2)
O(5)–Mo(2)–O(2)	159.5(3)	O(5^{I})–Mo(3)–O(34)	78.0(3)	Mo(3^{I})–O(5)–Mo(4)	98.2(2)	C(5)–C(6)–C(1)	120(1)
O(12)–Mo(2)–O(2)	100.0(4)	O(5)–Mo(4)–O(4)	161.1(3)	Mo(2)–O(12)–Mo(1)	118.0(5)	C(16)–C(11)–C(12)	123(2)
O(21)–Mo(2)–O(2)	105.5(4)	O(14)–Mo(4)–O(4)	100.8(4)	Mo(4)–O(14)–Mo(1)	118.0(4)	C(13)–C(12)–C(11)	122(2)
O(34^{I})–Mo(2)–O(2)	88.5(3)	O(34)–Mo(4)–O(4)	99.6(3)	Mo(3)–O(23)–Mo(2)	109.0(3)	C(12)–C(13)–N(4)	119(2)
O(23)–Mo(2)–O(2)	99.8(4)	O(41)–Mo(4)–O(4)	105.2(4)	Mo(4^{I})–O(23)–Mo(2)	104.1(3)	C(14)–C(13)–N(4)	127(2)
O(23)–Mo(2)–O(5)	73.8(3)	O(23^{I})–Mo(4)–O(4)	89.5(3)	Mo(4^{I})–O(23)–Mo(3)	108.5(3)	C(14)–C(13)–C(12)	111(2)
O(12)–Mo(2)–O(5)	78.9(3)	O(14)–Mo(4)–O(5)	78.6(3)	Mo(2^{I})–O(34)–Mo(3)	108.5(3)	C(15)–C(14)–C(13)	126(2)
O(21)–Mo(2)–O(5)	94.6(3)	O(34)–Mo(4)–O(5)	74.0(3)	Mo(2^{I})–O(34)–Mo(4)	104.6(3)	C(16)–C(15)–C(14)	118(2)
O(34^{I})–Mo(2)–O(5)	71.1(2)	O(41)–Mo(4)–O(5)	93.3(3)	C(7)–N(1)–C(6)	117(2)	C(11)–C(16)–N(3)	123(2)
O(21)–Mo(2)–O(12)	102.6(4)	O(34)–Mo(4)–O(14)	147.9(3)	C(8)–N(1)–C(6)	120(2)	C(15)–C(16)–N(3)	118(2)
O(23)–Mo(2)–O(12)	148.2(3)	O(41)–Mo(4)–O(14)	102.3(4)	C(8)–N(1)–C(7)	121(1)	C(15)–C(16)–C(11)	119(2)
O(34^{I})–Mo(2)–O(12)	84.5(3)	O(41)–Mo(4)–O(34)	95.9(3)	C(9)–N(2)–C(3)	114(2)		
O(23)–Mo(2)–O(21)	95.7(4)	O(23^{I})–Mo(4)–O(5)	71.6(2)	C(10)–N(2)–C(3)	120(2)		
O(34^{I})–Mo(2)–O(21)	162.7(4)	O(23^{I})–Mo(4)–O(14)	83.3(3)	C(10)–N(2)–C(9)	115(2)		

Symmetry code: I $-x, -y, -z$.

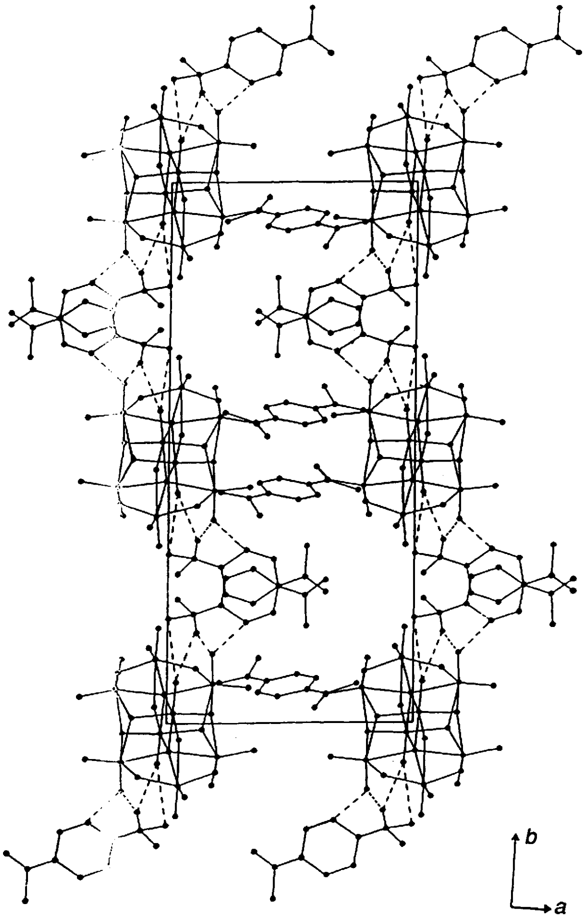

Fig. 5 Crystal packing of compound **1** projected along the [001] direction, showing the intermolecular interactions

both of these charged species. Therefore the two series of compounds have the general formulae β-$[\mathrm{Htmpd}]_x[\mathrm{tmpd}]_{4-x}[\mathrm{Mo_8O_{26}}]$ and β-$[\mathrm{Htmpd}]_x[\mathrm{tmpd}]_{3-x}[\mathrm{HMo_8O_{26}}]$ the only missing compound being the neutral salt containing just tmpd$^+$ ($x = 0$). Attempts to synthesize β-$[\mathrm{tmpd}]_4[\mathrm{Mo_8O_{26}}]$ proved unsuccessful even under photochemical conditions, only the related acid salt β-$[\mathrm{tmpd}]_3[\mathrm{HMo_6O_{26}}]$ being formed.

Generally speaking the above compounds are not interconvertible. In spite of this, they provide an interesting and unique example of the same organic component being present both as the cationic and donor component yielding the two extrema and an intermediate stage of a possible photochromic couple. Activation of this couple would require the choice of a suitable polyanionic component, *i.e.* a reversibly reducible type I polyanion,[27] possibly avoiding also the proton-transfer step necessary in this case.

Pertinent examples in the literature are rare and include salts of the type $[\mathrm{NEt_4}][\mathrm{ttf}]_6[\mathrm{PM_{12}O_{40}}]$ (ttf is the radical cation of tetrathiafulvalene) or $[\mathrm{NEt_4}]_5[\mathrm{Zn(tpp)}]_2[\mathrm{PM_{12}O_{40}}]$, M = Mo or W (tpp = 5,10,15,20-tetraphenylporphyrinate), which, beside the donor organic molecule, contain as a third component a redox-inactive counter ion.[7,28] These compounds fulfil some of the prerequisites pointed out above. However, the thermodynamic redox potentials are not properly tuned and forms containing only the one-electron-reduced (Mo) or the fully oxidized (W) polyanion are presently known.

The X-ray structural study of compound **1** was undertaken in order to obtain a more quantitative picture of the interrelations between the Htmpd$^+$ and tmpd$^+$ molecules and to verify the presence of a sizeable interaction between the organic donor and the inorganic acceptor. In agreement with spectroscopic and magnetic data the X-ray results show that the radical cations exist as tightly bound, discrete dimers. There are no interactions between the radical cations and the polyanions, as has already been found for related compounds.[2] The monoprotonated cations are linked instead by means of hydrogen bonds to the polyanions, as was previously found in the *N*,*N*-dimethylanilinium salt of $[\mathrm{Mo_8O_{26}}]^{4-}$.[25] In the case of compound **3** no structural information is available. However, spectroscopic and magnetic data for this compound suggest the unusual presence of isolated, non-interacting radical cations.

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