

Synthesis and Crystal Structure of a New Charge-Transfer Complex [(C₁₉H₁₈N₃)₂H][PMo₁₂O₄₀]

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Abstract. A new charge-transfer complex with tri-(*p*-aminophenyl)-carbonium cations was synthesized from the hydrothermal reaction of pararosanilin and (NH₄)₃[PMo₁₂O₄₀]·3H₂O, and was characterized with UV-vis, EPR and elemental analysis, as well as single crystal x-ray diffraction.

Keywords: Charge-transfer complex; Keggin structure; Pararos-anilin; crystal structure; EPR spectrum

Synthese und Kristallstruktur des neuen Charge-Transfer-Komplexes [(C₁₉H₁₈N₃)₂H][PMo₁₂O₄₀]

Inhaltsübersicht. Durch hydrothermale Reaktion von Pararos-anilin mit (NH₄)₃[PMo₁₂O₄₀]·3H₂O wurde ein neuer Charge-Transfer-Komplex mit Tri(*p*-aminophenyl)carbonium-Kationen synthetisiert

und charakterisiert mittels UV-VIS-, EPR-Spektroskopie und Elementaranalyse sowie durch Einkristall-Röntgenbeugung.

1 Introduction

Metal oxide clusters of polyoxometalates (POMs) have attracted great attention in recent years due to their versatility and utility in catalysis (e.g., photochemical dehydrogenations of organic substrates), medicine (e.g., anti-viral and anti-tumor drugs), and material sciences [1]. Of particular interest is the use of POMs as electron-accepting moieties in charge-transfer materials that are prepared by cocrystallization with organic donors [2]. This usage is based on (i) the good solubility of POMs in both aqueous and nonaqueous solutions, (ii) the possibility of varying the charges, shapes, and sizes of POMs that can induce new donor packings and, therefore, new band structures, (iii) the ability of POMs to act as electron reservoirs and (iv) the possibility of introducing magnetically active transition metal ions at specific sites of the POMs [3]. Some charge-transfer complexes of this class have been reported to show interesting metallic behavior, such as [ET]₅[VW₅O₁₉]·5H₂O [4] and [ET]₁₁[P₂W₁₈O₆₂]·3H₂O [5] (ET = bis(ethylenedithio)tetrathiafulvalene). Donors in those charge-transfer complexes include substituted amides [6], aromatic amines [7] and electron-rich substrates such as tetrathiafulvenes (TTF) [3], decamethylferrocene [3] and so on. All these donors have

planar conjugated π systems, which can stabilize the positive charge and reduce energy band gap. Many organic dyes, such as pararosanilin, methylviolet and malachite green, have a basic structure of triphenylcarbon group. This structure has a large planar conjugated π system and plenty of reactive sites that can be modified by functional groups. On the other hand, the flamboyant colors of these dyes show the potential electric and optic properties. But so far, no charge-transfer complex containing such dye donor has been reported. Here we report the synthesis and characterization of a new complex with dye cations of tri-(*p*-aminophenyl)carbonium and *Keggin* type polyanions.

2 Experimental

2.1 Preparation

[(C₁₉H₁₈N₃)₂H][PMo₁₂O₄₀] (**1**) was synthesized by the hydrothermal reaction of 0.16g (0.49 mmol) pararosanilin and 0.48g (0.25 mmol) (NH₄)₃[PMo₁₂O₄₀]·3H₂O in 15ml (0.83 mol) water at 180 °C for 3 days. Black crystals were filtered from blue solution, washed with water and dried in air. Weight 0.23 g, yield 38 %. Elemental analysis: C₃₈H₃₇Mo₁₂N₆O₄₀P₁ (Mr = 2400), C 19.1 (calc. 19.0); H 1.49 (1.54); Mo 47.8 (48.0); N 3.53 (3.50); P 1.32 (1.29) %.

2.2 X-ray crystallographic study

A blue block single crystal with dimensions 0.25mm × 0.12mm × 0.10mm was mounted on a Rigaku RAXIS-RAPID X-ray diffractometer. Diffraction data was collected at 173K with graphite monochromated MoK α radiation (λ = 0.071073nm) operating at

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Table 1 Selected bond lengths/Å

Mo1–O6	1.646(3)	Mo4–O18B	2.080(5)
Mo1–O9	1.819(3)	Mo4–O22	2.438(4)
Mo1–O7	1.830(3)	Mo4–O20 ^{a)}	2.482(4)
Mo1–O8	1.978(3)	Mo5–O2	1.647(3)
Mo1–O13 ^{a)}	1.987(3)	Mo5–O14A	1.807(5)
Mo1–O20	2.448(4)	Mo5–O8	1.844(3)
Mo1–O21 ^{a)}	2.452(4)	Mo5–O16A	1.911(5)
Mo2–O3	1.653(3)	Mo5–O14B	1.929(5)
Mo2–O16A	1.747(5)	Mo5–O10	1.996(3)
Mo2–O11	1.837(3)	Mo5–O16B	2.086(5)
Mo2–O16B	1.957(5)	Mo5–O19	2.438(4)
Mo2–O15A	1.959(5)	Mo6–O1	1.650(2)
Mo2–O9 ^{a)}	1.992(3)	Mo6–O12A	1.707(5)
Mo2–O15B	2.035(5)	Mo6–O15A	1.753(5)
Mo2–O19	2.410(4)	Mo6–O17B ^{a)}	1.867(5)
Mo3–O5	1.657(3)	Mo6–O14A	1.907(5)
Mo3–O18A	1.761(5)	Mo6–O12B	1.975(6)
Mo3–O10	1.814(3)	Mo6–O15B	2.003(5)
Mo3–O18B	1.950(5)	Mo6–O17A ^{a)}	2.083(5)
Mo3–O7	1.976(3)	Mo6–O14B	2.140(5)
Mo3–O12A ^{a)}	2.023(5)	Mo6–O19	2.466(4)
Mo3–O12B ^{a)}	2.043(5)	Mo6–O22 ^{a)}	2.497(4)
Mo3–O22	2.454(4)	P1–O21	1.507(4)
Mo3–O21 ^{a)}	2.502(4)	P1–O21 ^{a)}	1.507(4)
Mo4–O4	1.643(3)	P1–O20	1.509(4)
Mo4–O17B	1.845(5)	P1–O20 ^{a)}	1.509(4)
Mo4–O13	1.859(3)	P1–O22 ^{a)}	1.547(4)
Mo4–O18A	1.888(5)	P1–O22	1.547(4)
Mo4–O17A	1.894(5)	P1–O19	1.595(4)
Mo4–O11	1.946(3)	P1–O19 ^{a)}	1.595(4)

^{a)} Symmetry code: $-x+1, -y+1, -z+1$

50kV and 40mA. An absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program [8]. The structure was solved by direct methods and successive difference maps (SHELXS 97) [9] and refined by full-matrix least

squares on F^2 using all unique data (SHELXL 97) [10]. The non-hydrogen atoms were refined anisotropically.

$[(C_{19}H_{18}N_3)_2H][PMo_{12}O_{40}]$, Mr = 2400, triclinic, space group $P-1$ (No. 2), $a = 9.918(2)$, $b = 11.046(2)$, $c = 13.638(3)$ Å, $\alpha = 86.51(3)$, $\beta = 88.96(3)$, $\gamma = 78.48(3)^\circ$, $V = 1461.3(5)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 2.727$ gcm⁻³, $\mu(\text{Mo-K}\alpha) = 2.620$ mm⁻¹, 6592 independent reflections collected, 5965 observed for $I > 2\sigma(I)$ ($R_{\text{int}} = 0.0166$). $R_1 = 0.0253$ (observed data) and $wR_2 = 0.0592$ (all data) for 585 parameters.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union road, Cambridge CB2 1EZ, UK, deposition number CCDC 175926 (Fax: int.code+(1223)336-033; email: teched@chemcryst.cam.ac.uk).

3 Results and Discussion

Single crystal diffraction of complex **1** showed a sandwich structure with two tri-(*p*-aminophenyl)carbonium cations nipping a *Keggin* anion (Fig. 1). The spherical polyoxometalate anions and organic cations form an interval layer arrangement along the c direction. The whole structure has a pseudosymmetric center, which sits at the position of center P atom of the anion. The structural detail of the *Keggin* anion is similar to the typical ones [11–13]. The orientation of the central PO₄ tetrahedron has two possibilities, which are related by a centrosymmetric operation. Such circumstance of PO₄ tetrahedron can also be found in some other *Keggin* type complexes [13]. Twelve μ_2 oxygen atoms are disordered and each have two possible sites. The

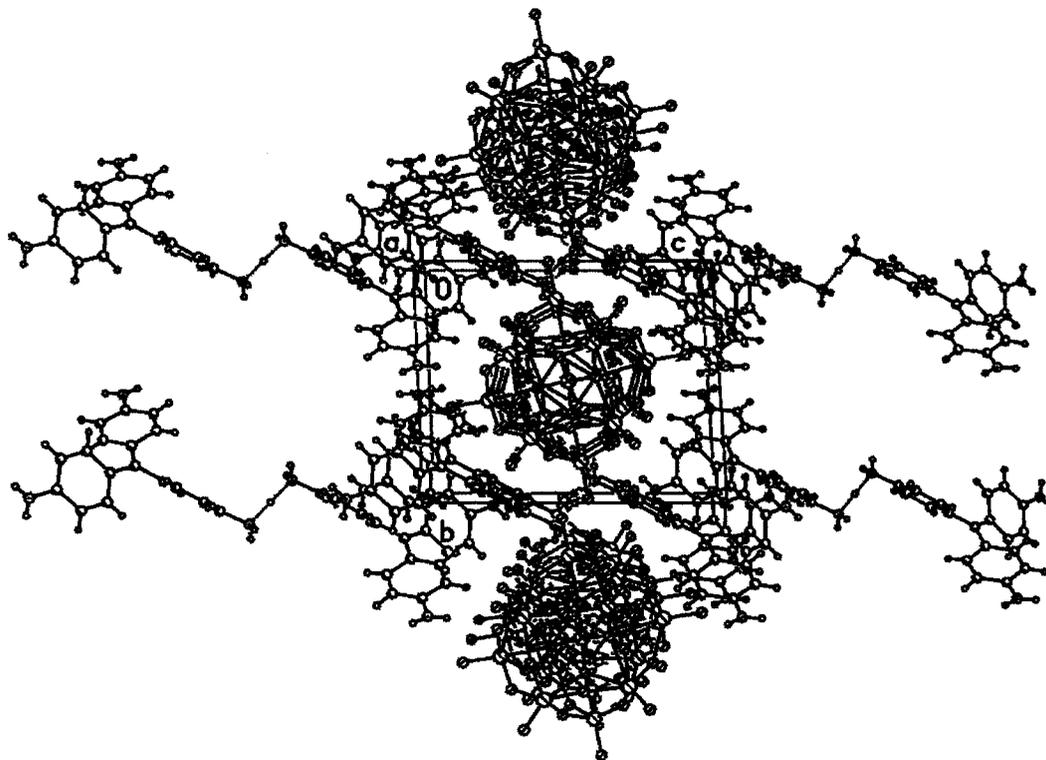


Fig. 1 The crystal structure of complex **1**

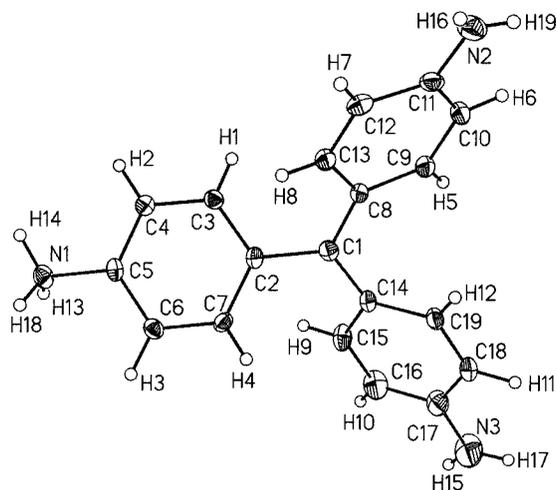


Fig. 2 The structure of organic cation in complex 1

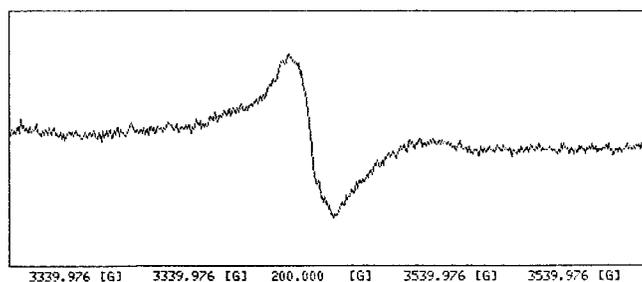


Fig. 3 The EPR spectrum of complex 1

organic cation has a propeller shape (Fig. 2), just like its shape in the crystal of a perchlorate described by Koh et al. [14]. The four central carbon atoms C1, C2, C8 and C14 are coplanar with a largest deviation from planarity of 0.016 Å. The individual benzene rings are also planar, and the amino nitrogen atoms lie very close to these planes. The three benzene rings are twisted out of the plane of the four central carbon atoms by angles of 37.9° for ring C2-C7, 29.8° for ring C8-C13 and 26.8° for ring C14-C19. The bond distances of the organic cation and polyanion are in the range of related compounds [11–15] and are not discussed further here.

From the differential Fourier map of electron density, an extra hydrogen atom (H13) is found at the midpoint of N1–N1A with occupancy of 0.5. The bond distance of N1–C5 is 1.442(4) Å, much longer than that of N2–C11 and N3–C17 (both are 1.348(5) Å). It indicates that one half of the donors are protonated, and the charge of the cations should be +1.5, averagely. This charge fits the –3 charge of Keggin polyanion. The EPR spectrum (Fig. 3) of complex 1 at room temperature gives a signal of $g = 1.98$, indicating the existence of unpaired electron. Since there is no unpaired electron in the initial cation (the EPR spectrum of pararosanilin shows no signal) and polyanion, this unpaired electron must be generated *via* a charge-transfer

mode, from the organic cation to the polyanion. The broadening of the EPR spectrum indicates that the electron is delocalized. This is typical of Class II mixed-valence compounds [16].

There are hydrogen bonds between cation and cation (N1–H13···N1 (symmetry code: $-x+2, -y, -z+1$), 2.877 Å, 180.0°) as well as cation and polyanion (N2–H19···O15B ($x, y, z+1$), 2.846 Å, 173.7°). The shortest contact distances between carbon atoms and anion oxygen atoms are 2.941 Å (C4···O11), 2.964 Å (C4···O1 ($-x+1, -y, -z+1$)), 3.008 Å (C3···O18B), 3.081 Å (C5···O1 (2656, $-x+1, -y, -z+1$)), 3.100 Å (C19···O6 (2667, $-x+1, -y+1, -z+2$)) and 3.146 Å (C18···O6 (2667, $-x+1, -y+1, -z+2$)), which are all shorter than the *van der Waals* distance (3.20 Å). These short contact distances enable a close interaction between donors and acceptors and therefore facilitate the charge transfer.

The UV-vis spectrum of $(NH_4)_3[PMo_{12}O_{40}] \cdot 3H_2O$ in DMF solution has two absorption bands at 267 nm and 306 nm, while that of pararosanilin has a very strong absorption band at 553 nm and a less strong band at 291 nm. The absorption of organic cations is so strong that the absorption of polyanions is covered in the spectrum of complex 1 and can only be noticed from the two shoulder peaks of the band at 291 nm. No IVCT band is observed. It indicates that, not like the circumstance in crystal state, complex 1 is very probably almost entirely dissociated in solution, so the interactions between organic cations and polyanions are very weak.

In conclusion, crystal structural analysis and EPR show the existence of charge transfer between tri-(*p*-aminophenyl)carbonium cations and Keggin polyanions. This is the first example of charge-transfer complex based on triphenylcarbon group and polyoxometalates. Further study is now taken in our laboratory on the physical properties of complex 1 and on the synthesis of other related complexes.

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