

Synthesis, Structure, and Characterization of Oxomolybdenum(V) Phthalocyaninato(2−) Triiodide

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Crystals of oxomolybdenum(V) phthalocyaninato(2−) triiodide, MoOPcI₃ (Pc = C₃₂H₁₆N₈^{2−}) have been obtained directly in the reaction of *o*-dicyanobenzene with molybdenum oxide under a stream of iodine at 210 °C. MoOPcI₃ crystallizes in space group *Cmcm* (No. 63) of the orthorhombic system with $a = 14.441(3)$ Å, $b = 15.194(3)$ Å, $c = 14.085(3)$ Å, and $Z = 2$. The crystals of MoOPcI₃ are built up from separate units of MoOPc⁺ and I₃[−], forming linear aggregates. The I₃[−] ions have been also detected by Raman spectroscopy. The magnetic susceptibility measurement versus temperature shows typical Curie–Weiss behavior. The effective magnetic moment ($\mu_{\text{eff}} = 1.72 \mu_{\text{B}}$) shows one unpaired electron. A single EPR line was observed. The value of g (1.9716) indicate that the unpaired electron is localized on molybdenum cation (d¹). The temperature dependence of the conductivity of MoOPcI₃ shows its metallic-like character ($d\sigma/dT < 0$). At room temperature the conductivity equals $(3.5–4) \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$. The charge transport proceeds mainly along linear (MoOPcI₃)_n aggregates.

Introduction

The phthalocyanine belongs to the group of the most versatile ligands, forming complexes with almost every metal of the periodic system.¹ However, the chemistry of molybdenum phthalocyaninates is still very underdeveloped. The molybdenum, having several oxidation states from +2 to +6, can form several different phthalocyanine complexes. The molybdenum phthalocyanine was first reported by Byrne et al.,² however, the authors did not give further information on the chemistry of this phthalocyanine. Some other authors have obtained the molybdenum phthalocyanine using the MoCl₅ and phthalonitrile in quinoline at 220 °C³ or using molybdenum and phthalonitrile.⁴ Shurvell and Pinzuti⁵ using the IR spectroscopy and Hill and Norgett⁶ from the mass and IR spectroscopy identified the oxomolybdenum phthalocyanine, MoOPc, and assigned the band at $\approx 972 \text{ cm}^{-1}$ in IR spectrum to the molybdenyl stretching ($\nu(\text{Mo}=\text{O})$).

The oxomolybdenum(IV) phthalocyaninato complex is the first molybdenum phthalocyanine complex, which was structurally characterized by X-ray diffraction on single crystal.⁷ The oxomolybdenum(IV) phthalocyanine has been found to be a very versatile precursor for the preparation of a series of new phthalocyaninato complexes of lower and higher valent molybdenum. The oxidation of oxomolybdenum(IV) phthalocyanine leads to the Mo(V) and Mo(VI) phthalocyaninato complexes.^{8–12} Di-

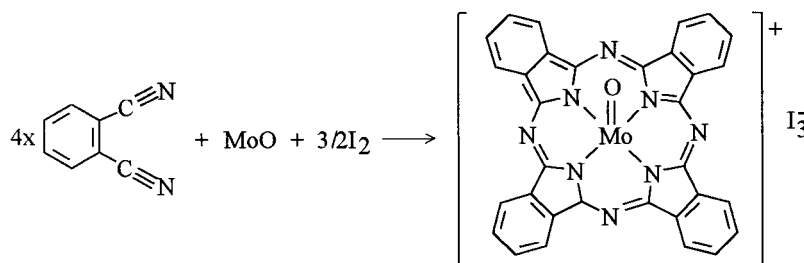
oxomolybdenum(VI) phthalocyanine, MoO₂Pc, has also been obtained by a direct reaction of dioxobis(acetyl acetate)-molybdenum(VI) with metal-free phthalocyanine.¹³ Homborg and co-workers have synthesized new complexes with 2+ and 3+ oxidation states of molybdenum.^{14,15} The cyclic and differential-pulse voltammetry of the Mo(III) phthalocyanine complex clearly showed two quasi-reversible cathodic processes, which have been assigned to the phthalocyaninato(2−) reduction (Pc^{2−}/Pc^{3−}) and to the reduction of the internal molybdenum cation (Mo³⁺/Mo²⁺).¹⁴ Recently, two new Mo(II) phthalocyaninato complexes were obtained by reduction of oxomolybdenum(IV) phthalocyanine.¹⁵ One of them is diamagnetic, and the other paramagnetic with $\mu_{\text{eff}} = 3.15 \mu_{\text{B}}$.

The aim of our work is obtaining a iodine-doped molybdenum phthalocyanine complexes. The iodine-doped phthalocyanine complexes are well-known as highly conducting materials. The high conductivity of the iodine-doped phthalocyanines can be explained (1) by the interaction of the neighboring π ligand orbitals, as in the organic molecular metals and (2) by linear chains of the metal spine, that propagate charge through metal-based a_{1g} (d_{z²}) orbitals.^{16–18} Using a slightly modified method¹⁹ we have obtained several iodine-doped phthalocyanines. Additionally, it has been stated that iodine-doped atoms can be directly bonded to the internal metal cation yielding mono-^{20,21}

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Scheme 1



and diiodometallophthalocyanines (cis or trans position).^{22–24} Moreover, the iodine-doped atoms can form the neutral I₂ molecules as bridge molecules for dimerization or polymerization of iodo- or diiodometallophthalocyanines.^{25,26} However, the iodine atoms in most of iodine-doped phthalocyanines exist as the triiodide I₃[−] ions,^{27–29} which form the linear chains. Their resonance Raman spectra are typical for the compounds containing the symmetrical triiodide ions.^{29–32}

The present paper describes structure and some properties of new iodine-doped oxomolybdenum phthalocyanine, MoOPcI₃.

Experimental Section

Synthesis. The crystals of oxomolybdenum(V) phthalocyaninato(2−) triiodide, [MoOPc]I₃ (Pc = C₃₂H₁₆N₈^{2−}), were obtained directly by the reaction of molybdenum oxide (MoO) and 1,2-dicyanobenzene (C₆H₄(CN)₂) under a stream of iodine. The powder molybdenum oxide, 1,2-dicyanobenzene, and iodine (in a molar proportion 1:4:3, with about 5% excess of 1,2-dicyanobenzene and iodine in relation to molybdenum oxide) were mixed together and pressed into pellets. The pellets were inserted into an evacuated glass ampule and sealed. The ampule was heated at 210 °C for 1 day. At this temperature (210 °C) the liquid 1,2-dicyanobenzene undergoes catalytic (by molybdenum oxide) tetramerization forming the phthalocyaninato(2−) skeleton, with the transfer of the two electrons from molybdenum to the formed phthalocyaninato unit. Simultaneously the oxidation process of molybdenum by iodine atoms present in the reaction is continued, yielding good-quality crystals of the molybdenum(V) phthalocyaninato complex (see Scheme 1). The elemental analysis has been made on an energy dispersive spectrometer. Found: Mo, 9.55; I, 37.84; C, 38.22; N, 11.17; O, 1.64; H, 1.58. Calcd for MoOC₃₂H₁₆N₈I₃: Mo, 9.54; I, 37.87; C, 38.24; N, 11.15; O, 1.60; H, 1.60.

X-ray Data Collection. A black-violet parallelepipedal single crystal of [MoOPc]I₃ having a mean edge of 0.20 mm was used for data collection on a four-circle KUMA KM4 diffractometer equipped with a graphite monochromator and Mo K α radiation. Preliminary examination of the crystal by rotation and Weissenberg photographs indicated the orthorhombic system and C-centered space group. The unit cell parameters were refined by least-squares method fit of 30 centered reflections measured in the 2 θ range 17–24°. The intensities of a total 4630 reflections in the range 4 < 2 θ < 64° using the ω -2 θ scan were measured. Two standard reflections were monitored every 50. They showed no significantly intensity variation (\approx 0.8%). Intensities and their standard deviations were corrected for Lorentz and polarization effects. Face indexed analytical absorption and extinction correction

Table 1. Crystallographic Data for MoOPcI₃

empirical formula	MoOPcI ₃
mol wt	1005.17
cryst syst	orthorhombic
space group	<i>Cmcm</i> (No. 63)
unit cell dimensions, Å	
<i>a</i>	14.441(3)
<i>b</i>	15.194(3)
<i>c</i>	14.085(3)
volume, V [Å ³]	3090.5(11)
<i>Z</i>	4
<i>D</i> _{calcd} , g/cm ³	2.160
<i>D</i> _{obs} (measd, flotation), g/cm ³	2.15
radiation, Mo K α , [Å]	λ = 0.710 73
absorption coefficient, μ [mm ^{−1}]	3.463
<i>R</i> ^a	0.0230
w <i>R</i> (<i>F</i> ²) ^b	0.0592

$$^a R = \sum ||F_o| - |F_c|| / \sum F_o, \quad ^b wR(F^2) = \{ \sum (w(F_o^2 - F_c^2)^2) / \sum wF_o^4 \}^{1/2};$$

$$w^{-1} = [\sigma^2(F_o^2) + (0.0348P)^2], \quad \text{where } P = (F_o^2 + 2F_c^2)/3.$$

were applied.³⁴ The min and max transmission factors are 0.391 48 and 0.715 25, respectively. The extinction coefficient equals 0.001 15(5); 2442 independent reflections (2029 with $I > 2\sigma_I$, $R_{int} = 0.0211\%$) were used for the structure solution and refinement.

Structure Solution and Refinement. The structure was solved by the Patterson heavy-atom method, which revealed the positions of the molybdenum and iodine atoms. The remaining atoms were located subsequently from difference Fourier synthesis. The structure was refined with anisotropic thermal parameters by full-matrix least-squares method, using the SHELXL97 program.³⁵ Hydrogen atoms of the phenyl rings introduced in the structure factor calculations by their geometrical coordinates (HFIX 43) with the $U_{iso} = 1.2U_{iso}$ (i.e. 20% higher than the carbon atoms directly bonded the H atom). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/[\sigma^2(F) + (0.03489P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The final unweighted and weighted agreement factors converged to $R = 0.0230$ and $wR(F^2) = 0.0560$, a goodness of fit calculation resulted in a value of 1.028 at final convergence. The final difference map calculation showed no peaks of chemical significance; the largest were +0.59 and −0.94 e/Å³. Scattering factors for neutral atoms and corrections for anomalous dispersion were as given in the SHELX97 program.³⁵ Final agreement factors and crystallographic data are given in Table 1. Selected bond lengths and angles are collected in Table 2.

Raman Spectroscopy. The Raman spectra were recorded at room temperature on a Jobin-Yvon Ramanor U-1000 spectrometer equipped with photomultiplier-type detector and phonon-counting hardware. The 90° geometry was used. An argon-ion laser line at 514.5 nm, of power 100 mW, was used as exciting radiation. Resolution was set up to 3 cm^{−1}.

Magnetic Susceptibility Measurements. The temperature dependence of the magnetic susceptibility of [MoOPc]I₃ was recorded from 300 to 1.8 K with a Quantum Design SQUID magnetometer (San Diego, CA). Data were recorded at magnetic field of 0.5 T on a sample of 20 mg.

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Table 2. Selected Bond Distances (Å) and Angles (deg)^a

I1–I2	2.9736(7)
I2–I3	3.1934(7)
Mo1–O1	1.748(3)
Mo1–N2	2.0136(14)
O1–Mo1–N2	107.50(4)
N2–Mo1–N2 ⁱ	145.00(9)
N2 ⁱ –Mo1–N2 ⁱⁱ	82.11(8)
N2–Mo1–N2 ⁱⁱ	87.50(8)

^a Symmetry code: (i) $-x, y, 1/2 - z$; (ii) $x, y, 1/2 - z$.

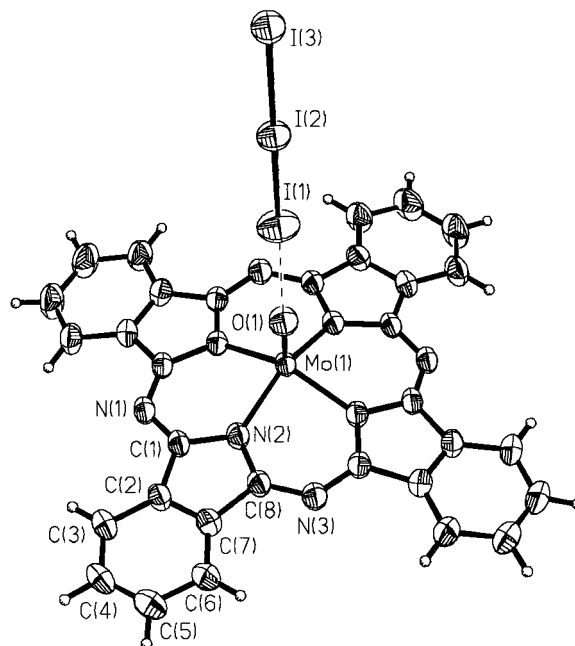
Electron Paramagnetic Resonance Measurements. EPR measurements were made on SE-Radiopan and ESP 300 E-Bruker X-band spectrometers at room temperature. The studies were carried out on solid samples of 2–7 mg. A single-line EPR spectrum at $g = 1.9716$ was observed for $[\text{MoOPc}]_3$. The concentrations of the free radicals in the $[\text{MoOPc}]_3$ samples were calculated using standard integration of the derivative signal and by comparing the area of the free radical EPR signal with the area determined with the free radical standard (DPPH, TEMPO, TEMPOL, and Rickitt's ultramarine). The calculation of the sum of spin concentration is 6.02×10^{20} spins/g, i.e., $\cong 1$ unpaired electron per $[\text{MoOPc}]_3$ molecule.

Conductivity Measurement. Conductivity measurements were carried out on the polycrystalline compacted samples (pressed into pellets, $\sim 10^5$ kPa) by using a standard four-point probe technique³⁶ with a sampling current of 20 μA . Variation of the temperature was achieved by placing the sample in a cold-gas stream (N_2 or He).

Results and Discussion

This study is a part of our investigation on synthesis and characterization of the iodine-doped metallophthalocyanines. Earlier we reported that, besides the known iodine-doped phthalocyanines, in which the iodine-doped atoms form chains of the disordered symmetrical triiodide ions I_3^- , the iodine-doped atoms can be directly joined to the central metal ion^{23–25} and simultaneously can form a neutral molecule of I_2 which is a bridge for dimerization or for developing a polymeric form of mono- and diiodometallophthalocyanine complexes.^{26,27} This paper is the first to report the X-ray structure and characterization of iodine-doped phthalocyanine, in which the iodine-doped atoms form ordered unsymmetrical triiodide ions. The MoOPcI_3 complex is a black-violet species stable at room temperature. Although it has been mentioned that the oxidation of the Mo^{IV} -OPc by iodine yields the complex MoOPcI_x with the iodine index ranging from 1.4 to 2.6 and that the iodine-doped atoms are probably disordered,⁷ our present investigation clearly shows that iodine-doped atoms with the iodine index equal to 3 are ordered in the crystal.

The molecule of MoOPcI_3 has $mm2$ symmetry and is nonplanar (Figure 1). The molybdenum cation coordinates the four nitrogen atoms of the phthalocyaninato(2–) ligand and the oxygen atom in axial position, forming a square pyramidal coordination. The molybdenum atom lies above the phthalocyaninato(2–) plane. The deviation of the Mo cation from the plane defined by the four isoindole nitrogen atoms equal to 0.605(5) Å in the direction to the axial oxygen atom. For a comparison the deviation of Mo cation in noniodinated oxomolybdenum(IV) phthalocyanine equals to 0.69 Å.⁷ The smaller deviation of the Mo cation from the N_4 plane in MoOPcI_3 is likely due to the greater interaction of the more positive molybdenum cation (5+) with the phthalocyaninato(2–) ligand in relation to the MoOPc , in which the Mo has a formal oxidation state of 4+. Similar deviations of the Mo cation can

**Figure 1.** View of the MoOPcI_3 and labeling scheme. Displacement ellipsoids are shown at the 50% probability level.**Table 3.** Coordination of the Central Ion of Oxometallophthalocyanine Complexes

compound	M–N [Å]	M=O [Å]	deviation of the metal from N_4 plane [Å]	ref
MoOPcI_3	2.0136(14)	1.748(3)	0.605(1)	this work
MoOPc	2.041	1.668(6)	0.69	7
TiOPc (monoclinic)	2.066	1.650(4)	0.70	39, 40
TiOPc (triclinic)	2.067	1.626(7)	0.72	39, 40
VOPc	2.026(7)	1.580(3)	0.575	41

be found in oxomolybdenum(IV) and oxomolybdenum(V) porphyrin derivatives.^{37,38} For a comparison the deviation of the central metal in the other oxometallophthalocyanines equals to 0.72 and 0.70 Å for the oxotitan(IV) phthalocyanine in the triclinic and monoclinic form,^{39,40} and 0.575 Å in vanadyl phthalocyanine⁴¹ (see also Table 3). The coordination of the Mo atom by phthalocyaninato(2–) ligand leads to its saucer shape. The largest deviation of the C(4) and C(5) atoms from the N_4 plane equals to 0.774(4) and 0.634(4) Å, respectively. The C–C and C–N bond lengths and angles for chemically equivalent bonds in the Pc ring agree well with those in other metallophthalocyanines, and are typical for the conjugated π electron system. The Mo–N distances of 2.014(2) Å in MoOPcI_3 are slightly shorter than those in MoOPc ⁷ and in oxomolybdenum(IV) porphyrin³⁷ but are comparable to those observed in oxomolybdenum(V) porphyrin derivatives.³⁸ The Mo–N distance closely correlates with the deviation of the Mo atom from the N_4 isoindole plane.

The Mo–O distance of 1.748(3) Å in MoOPcI_3 is longer than the one in undoped oxomolybdenum phthalocyanine.⁷ The value of Mo–O distance is evidence for the existence of π bonds with the bond order greater than 2. It should be added that in

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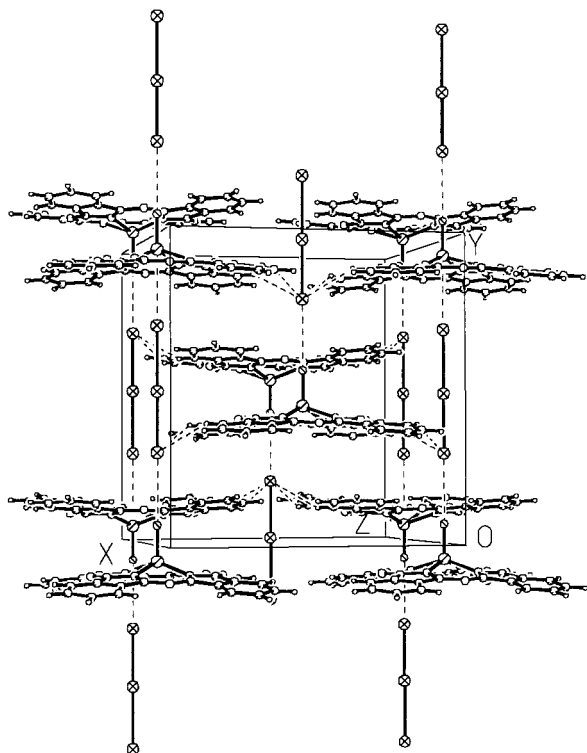


Figure 2. Arrangement of MoOPcI₃ molecules in unit cell. Hydrogen (I···H) interactions in the layer between the pseudo monodimensional aggregates of (MoOPcI₃)_n are shown as dashed lines.

the overlapping with the p orbitals of oxygen participate both orbitals (d_{xz} and d_{yz}) of Mo ion in equal degree. For a comparison the Mo–O bond length equals 1.656(6) and 1.655(10) Å in oxomolybdenum(IV) and -(V) porphyrin derivatives, respectively.^{37,38}

In contrast to the well-known tetragonal form of iodine-doped metallophthalocyanines and diphthalocyanines, in which the iodine-doped atoms develop a chains of disordered symmetrical triiodide ions, in MoOPcI₃ the iodine atoms form unsymmetrical I₃[−] ions, which can be also described as a donor–acceptor or hypervalent I–I₂ interaction. The latter is useful for describing the interaction in trihalide ions, i.e., electron-rich three-center bonding. Recently, for understanding the bonding in the I₃[−] ion in more details, the theoretical calculations using qualitative molecular orbital theory have been performed.⁴² The I–I₂ bonding energy in I₃[−] ion has been calculated to be 37.5 kcal/mol, and the calculated charge in the symmetrical I₃[−] ion gave −0.419 for two terminal iodines and −0.163 on the central atom. The calculated bond lengths in I₃[−] are approximately 0.3 Å longer than the bond length in an optimized neutral diiodide molecule (2.86 Å).⁴² Since the I₃[−] ions in the crystal of MoOPcI₃ are located between two neighboring [MoOPc]⁺ units and are electrostatically interacting with two oppositely charged atoms of the MoOPc units (Mo and O), in this crystal, the I₃[−] ions are unsymmetrical. The distance of the terminal iodine atom (I1) of the I₃[−] ion interacting (repulsive force) with axially coordinated oxygen atom of [MoOPc]⁺ unit (O1···I1) equal to 3.530(3) Å, while the other (I(3)) interacting (attraction force) with the molybdenum cation of the neighboring [MoOPc]⁺ unit (Mo···I3) distance equal to 3.7492(7) Å (Figure 2). The I–I distances in I₃[−] ion are equal to 2.9736(7) and 3.1934(7) Å. The shorter I–I bond distance in this unsymmetrical I₃[−] ions is longer than in pure iodine (2.662 Å in I₂ gaseous⁴³ and 2.765–(6) Å in solid state at −163 °C⁴⁴). One of the I–I bond distances in the I₃[−] ion in the MoOPcI₃ crystals is comparable, whereas

the other is longer in relation to those in iodine-doped metallophthalocyanines and diphthalocyanines.^{25,28,29,45} Recently, the presence of unsymmetrical triiodide I₃[−] ions in the “stapled” niobium(IV) diphthalocyanine complex has been reported⁴⁶ but both I–I bonds are significantly shorter (2.818(2) and 2.991(2) Å) than in MoOPcI₃.

The crystals of the MoOPcI₃ complex are built up from a separate units of [MoOPc]⁺ and I₃[−]. The mutual arrangement of MoOPcI₃ molecules in the unit cell (Figure 2) shows that the molecules of MoOPcI₃ form linear aggregates in which the two opposite units (MoOPc⁺ and I₃[−]) interacting electrostatically. These linear aggregates are parallel to the [010] direction in the crystal and have two opposite orientations (in the direction +y or −y). The linear aggregates of the same orientation are interconnected by a weak I···H hydrogen bonds (the I···H distance equal to 3.210(5) Å) and form a two-dimensional sheet (Figure 2). The sheets of MoOPcI₃ molecules in the crystal are interacting by the van der Waals forces.

Although the crystals of MoOPcI₃ are built up from the opposite MoOPc⁺ and I₃[−] ions, the compound no possesses the characteristic properties of the ionic crystals. The solubility of this compound in the most polar solvent is insignificant. As can be seen from the crystal structure architecture of the MoOPcI₃ both hydrophilic parts of this complex in the crystal are surrounded by a hydrophobic peripheral phenyl rings of the Pc macrocycle.

The Raman spectrum (Figure 3) of the species in the region 300–100 cm^{−1} shows only one intense peak located at ~109 cm^{−1}, with the characteristic overtone progression of the peak at ~220 cm^{−1}. This band system is unequivocally indicative of the presence of the I₃[−] ions in the crystal. This pattern is characteristic for linear triiodide ions detected also in other iodine-doped phthalocyanines.^{25,28,29,45}

The EPR spectrum of the solid state of MoOPcI₃ at room temperature exhibits a single strong signal at $g = 1.9716$, significantly lowered as the g parameter for the free electron (2.0023). Integration of this signal results in one electron per MoOPcI₃ molecule. The value of g parameter clearly shows that unpaired electron is localized on the Mo cation; thus the molybdenum atom in this complex has an oxidation state of 5+, which has one d electron. In the well-known tetragonal, partially oxidized phthalocyanines, the free electron is usually delocalized on a Pc ligand or over two Pc ligands in diphthalocyanines.^{25,28,29,45,47} The value of the g parameter indicates the location of the electron on the d orbital of the Mo central atom and is comparable to the one observed in the other oxomolybdenum(V) complexes.^{48,49} The natural molybdenum contains about 25% the nuclei ⁹⁵Mo and ⁹⁷Mo, with $I = 5/2$,

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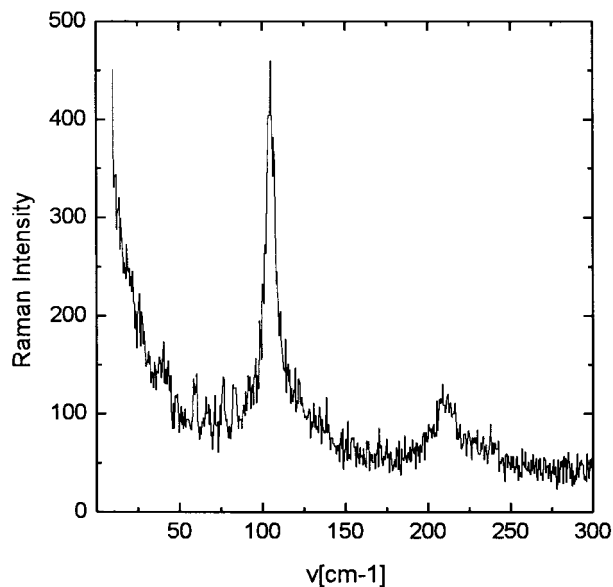


Figure 3. Resonance Raman spectra of polycrystalline samples of MoOPcI₃ at room temperature.

therefore the six hyperfine lines for the pentavalent molybdenum complexes in solution are observed.⁴⁸ In this complex, the EPR spectrum was carried out on solid species and hyperfine structure was not observed. This is typical for species containing a very high spin concentration.

Figure 4 shows the plot of the inverse molar susceptibility versus temperature for MoOPcI₃. Typical Curie–Weiss behavior is observed with no observable magnetic ordering down to 2 K ($\Theta \cong -4$). The effective magnetic moment, temperature independent, was equal to $1.72 \mu_B$, due to the one unpaired electron, which was also detected by EPR spectroscopy. Magnetic moments ranging from 1.65 to $1.73 \mu_B$ have been observed for other oxomolybdenum(V) complexes.⁴⁹

The four-probe conductivity measurement of polycrystalline sample of MoOPcI₃ at room-temperature is in the range $(3.5-4) \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$. This is an order of magnitude smaller than the conductivities for the most partially oxidized by iodine metallophthalocyanine like compounds $M^{II}Pc(I_3)_{1/3}$ ^{45,50} but is about 10^6 higher than the conductivity of the undoped MoOPc complex.⁷ Figure 5 shows the temperature response of the conductivity for a compacted polycrystalline sample of MoOPcI₃ over the range 20–300 K. There is a metallic-like dependence in conductivity ($d\sigma/dT < 0$) throughout the temperature range. The metallic character of conductivity has been also observed for other iodine-doped metallophthalocyanines. As can be seen from the crystal structure, we suggest that the charge transport mainly proceeds along the monodimensional aggregates.

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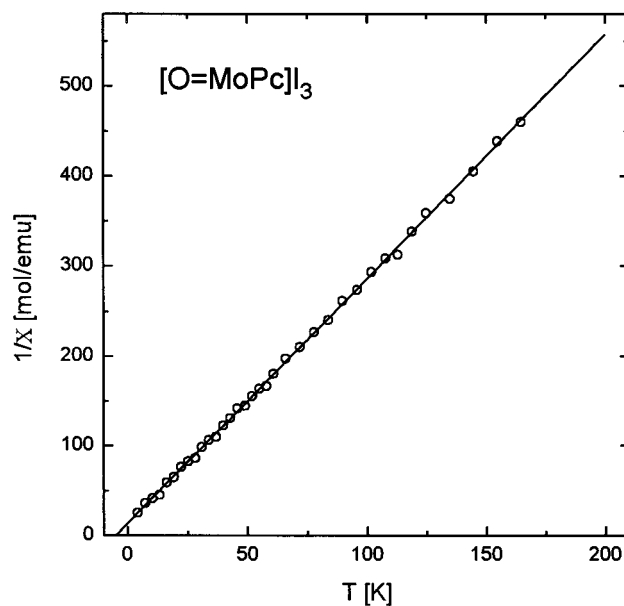


Figure 4. Plot of inverse molar susceptibility versus temperature for MoOPcI₃.

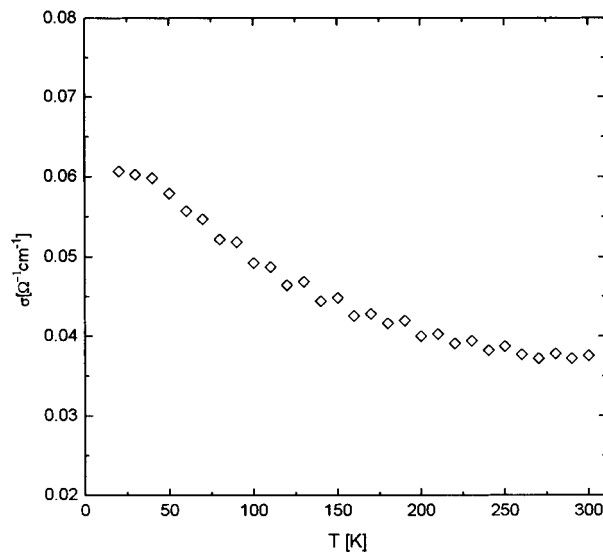


Figure 5. Temperature dependence of the conductivity of polycrystalline sample of MoOPcI₃.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, bond lengths and angles, and anisotropic temperature factors, in CIF format, are available free of charge via the Internet at <http://pubs.acs.org>.