High Intensity Trip-Multiplet Transitions, a Reality! Synthesis, Properties, and Crystal Structure of *l*-Bis(triphenylphosphine)iminium *trans*-Dibromophthalocyaninato(2–)molybdate(III)

Mathias Gorsch, Arne Kienast, Heiner Hückstädt, and Heiner Homborg*

Kiel, Institut für Anorganische Chemie der Christian-Albrechts-Universität

Received March 14th, 1997.

Abstract. Oxophthalocyaninato(2-)molybdenum(IV), activated by bromine oxidation prior to use, reacts with fused triphenylphosphine in the presence of bis(triphenylphosphine)iminium bromide to yield *linear*-bis(triphenylphosphine)iminium trans-dibromophthalocyaninato(2-)molybdate(III), ¹(PNP)^{trans}[Mo(Br)₂pc²⁻]. It crystallizes triclinic with crystal data: a = 10.506(1) Å, b = 12.436(2) Å, c = 12.918(2) Å, $\alpha = 76.186(1)^{\circ}$, $\beta = 67.890(1)^{\circ}$, $\gamma = 68.689(1)^{\circ}$; space group P1 (No. 2); Z = 1. Mo^{III} is in a pseudo-octahedral coordination geometry with the bromo ligands in transarrangement. The Mo–N_p and Mo–Br distance is 2.043(10) and 2.588(1) Å, respectively. The PNP cation adopts a *linear* conformation. In the IR spectrum ν_{as} (Mo–Br) is observed at 218 cm⁻¹ and ν_{as} (P–N) of the *linear* (P–N–P) core at 1406 cm⁻¹. Cyclic and differential-pulse voltammetry show two quasi-reversible cathodic processes at -1.15 and -0.53 V vs. Ag/AgCl. The first is assigned to a phthalocyaninate di-

rected reduction (pc^{2-}/pc^{3-}) , while the latter arises from a Mo directed reduction (Mo^{III}/Mo^{II}) . Spectral monitoring confirms the reversible Mo^{III}/Mo^{II} reduction. Two quasi-reversible anodic processes at 0.60 and 1.27 V are assigned to the successive Mo directed oxidation with redox couples Mo^{III}/Mo^{IV} and Mo^{IV}/Mo^{V} . For the first time, three very intense spin-allowed trip-quartet transitions are observed in the electronic absorption spectra at 7140 (TQ1), 16890 (TQ2) and 18700 cm^{-1} (TQ3) together with a sing-quartet transition at 15850 cm^{-1} and characteristic "Q" region with maximum at 28500 cm^{-1} and "N" region at 37400 cm^{-1} . All electronic excitations are of comparable intensity. A prominent low temperature emission at 6690 cm^{-1} is assigned to a spin-forbidden trip-sextet.

Keywords: Phthalocyaninate(2–); Molybdate(III); Crystal Structure; Optical Spectra

Trip-Multiplett Übergänge hoher Intensität, eine Realität! Synthese, Eigenschaften und Kristallstruktur von *l*-Bis(triphenylphosphin)iminium*trans*-dibromophthalocyaninato(2–)molybdat(III)

Inhaltsübersicht. Oxophthalocyaninato(2-)molybdän(IV), welches zuvor durch Oxydation mit Brom aktiviert worden ist, reagiert mit geschmolzenem Triphenylphosphin in Gegenwart von Bis(triphenylphosphin)iminiumbromid zu *line-ar*-Bis(triphenylphosphin)iminium-*trans*-dibromophthalocyaninato(2-)molybdat(III), ^{*l*}(PNP)^{trans}[Mo(Br)₂pc²⁻]. Dieses kristallisiert triklin mit den Zellkonstanten a = 10,506(1) Å, b = 12,436(2) Å, c = 12,918(2) Å, $\alpha = 76,186(1)^{\circ}$, $\beta = 67,890(1)^{\circ}$, $\gamma = 68,689(1)^{\circ}$; Raumgruppe P1 (No. 2); Z = 1.

Dr. H. Homborg Institut für Anorg. Chemie Olshausenstr. 40 D-24098 Kiel Fax: Int. + 4 31-8 80 15 20 e-mail: NAC74@RZ.UNI-KIEL.d400.de Mo^{III} befindet sich in pseudo-oktaedrischer Umgebung und koordiniert zwei trans-ständigen Bromoliganden. Der (Mo-N_p)- und (Mo-Br)-Abstand beträgt 2,043(10) und 2,588(1) Å. Das Kation liegt in linearer Konformation vor. Im IR-Spectrum beobachtet man v_{as} (Mo-Br) bei 218 cm⁻¹ und $v_{as}(P-N)$ des linearen (P-N-P)-Gerüstes bei 1406 cm⁻¹. Das zyklische und Differenz-Puls Voltammogramm zeigen zwei quasi-reversible kathodische Prozesse bei -1,15 und -0,53 V (gegen Ag/AgCl). Der erste Prozeß wird der Phthalocyaninat-Reduktion (pc^{2-}/pc^{3-}) , der zweite in Übereinstimmung mit spektroskopischen Daten der Mo-gerichteten Reduktion (Mo^{III}/Mo^{II}) zugeordnet. Zwei weitere quasi-reversible anodische Prozesse bei 0,60 und 1,27 V werden der sukzessiven Mo-Oxydation mit den Redoxpaaren Mo $^{\rm III}/$ Mo $^{\rm Iv}$ und Mo $^{\rm Iv}/Mo^{\rm V}$ zugeordnet. Erstmalig beobachtet man in den optischen Spektren neben einem Sing-Quartett-Übergang bei 15850 cm⁻¹, der charakteristischen "Q"-Region mit Maximum bei 28500 cm⁻¹ und "N"-Region bei 37400 cm⁻¹ drei sehr intensive spinerlaubte Trip-Quartett-

^{*} Correspondence Address:

Übergänge bei 7140 (TQ1), 16890 (TQ2) und 18700 cm^{-1} (TQ3). Alle elektronischen Anregungen sind von vergleichbarer Intensität. Eine bemerkenswerte Tieftemperatur-Emis-

Introduction

During the past two decades, great world-wide effort has elaborated a wealth of fascinating properties of phthalocyaninates. From this unique class of "new materials" future potential applications are expected for use in catalysis, chemical sensors, molecular metals and semiconductors, information technology, solar energy conversion and storage or photodynamic therapy. Current knowledge of some of these properties and applications has been covered into a series of monographs [1]. Besides, academic aspects are as well very important counterbalancing and completing the intense bio-inorganic research activities based on porphyrinates. It is in this area of phthalocyaninate chemistry that our emphasis concentrates on synthetic strategies of new tailor-made phthalocyaninates to elucidate subjects of considerable speculation and longstanding debate.

Presently, we wish to contribute to a better understanding of the electronic absorption spectra of phthalocyaninates in their standard pc^{2-} oxidation state, recently reviewed [2]. The beautiful blue and green colour, the most important attribute establishing phthalocyaninates as dyestuffs par excellence, arises from a very strong, isolated and small-banded absorption located in the red of the visible followed by a set of much less intense transitions in the blue. In many phthalocyaninates these so-called $\pi \rightarrow \pi^*$ transitions are localized to the pc²⁻ ligand alone. Because of the phthalocyaninate aza-bridges, the two highest occupied molecular orbitals $(a_{1u} > a_{2u}; D_{4h} \text{ symmetry})$ are inverted when compared with standard porphyrinates like tetraphenylporphyrinates or octaethylporphyrinates. As a consequence the extinction coefficient ε of the first singlet-singlet transition of phthalocyaninates is up to 100 times that of porphyrinates. Intriguing "irregular" spectral properties are observed for phthalocyaninates of open-shell, paramagnetic metal ions, features that are to a much smaller extent apparent in the corresponding porphyrinate spectra as well. These deviations from the "normal D_{4h} spectrum" of closedshell metal ions have been classified as "allo" or "hypso" and "hyper" spectra [3]. More precisely, most of the "irregularities" are routinely proposed to arise from charge transfer (CT) transitions. These are a second very multifaceted series of electronic excitations supposed to be present in phthalocyaninate/porphyrinate (p) spectra. They are classified as $p \rightarrow MCT$, $M \rightarrow pCT, L \rightarrow MCT, M \rightarrow LCT, and X \rightarrow MCT$ (L, X: axial ligands like pyridine (L) or halides (X)) to acsion bei 6690 cm^{-1} wird dem spinverbotenen Trip-Sextett-Übergang zugeordnet.

count for their direction and solvent and axial ligation effects.

In addition to these two classical allowed electronic excitations, there is a third type that involves spin-spin coupling of the π , π^* states of different multiplicities of the macrocyclic ligand with those of open-shell metal ions. A theoretical treatment of these so-called trip-multiplet (TM) transitions has been provided by Cory and Zerner in 1991, and reference is made to this very complete and detailed discussion [4]. Actually, TMs are by far the most "exotic" kind of allowed electronic excitations. They are generally weak, and vet still difficult to treat accurately by modern sophisticated calculations. Accordingly, TMs have been simply rejected by most of the scientific community, or are mistaken for the aforementioned CTs, substantiated by not unequivocal correlations with known (or estimated) electrode potentials [5]. This general opinion is distinctly opposite to our recent results pointing to an abundant presence of TMs in spectra of phthalocyaninates (and porphyrinates) of the paramagnetic transition metal ions of for instance Cr^{II} [5, 6], Cr^{III} [5, 7], Mn^{II} [8], Mn^{III} [8b, 9], Fe^I [10], and Fe^{III} [11] in their different spin states. It is the aim of the present discussion of the spectroscopical properties of *trans*-dibromophthalocyaninatomolybdate(III), the first pc²⁻ complex of Mo^{III}, to add further convincing experimental evidence that high intensity TMs are a reality.

Results and Discussion

Synthesis and Properties

The chemistry of phthalocyaninates of molybdenum is still very underdeveloped. Only a few oxo-complexes of higher valent molybdenum [12] and a diphthalocyaninate [Mo(pc²⁻)₂]Cl [13] are known. Oxophthalocyaninatomolybdenum(IV), $[Mo(O)pc^{2-}]$ has been found to be a very versatile precursor for the preparation of a series of new phthalocyaninates of low valent molybdenum. It is obtained as the main product by the reaction of ammonium heptamolybdate with boiling phthalodinitrile. However, nitridophthalocyaninato-molybdenum(V), $[Mo(N)pc^{2-}]$, with its distinctive infrared active Mo-N stretching vibration at 1030 cm⁻¹, is always present as a by-product, the oxidative deprotonation of the ammonium ion being the source of the nitrido ligand. Both complexes are (partially) oxidized by bromine to yield $[Mo(X)(Br)_x pc^{2-}]$ (X = O, N; $x \approx 2$). Because of interstitial incorporation of yet unknown bromine species, a characteristic property of many phthalocyaninates [14], the variable amount of bromine is always significantly higher than expected for a one electron oxidation of Mo. On the other hand, no ring oxidation has been detected by standard IR and UV-VIS techniques. These "activated" Mo complexes are distinctly more reactive than their Reaction of $[Mo(O)(Br)_xpc^{2-}]$ precursors. with triphenylphosphine in the presence of fused bis(triphenylphosphine)iminium bromide ((PNP)Br) vields crystalline linear-bis(triphenylphosphine)iminium trans-dibromophthalocyaninato(2-)molybdate(III), $^{l}(PNP)^{trans}[Mo(Br)_{2}pc^{2-}]$ (eq. (1)).

$$[Mo(O)(Br)pc^{2-}] + PPh_3 + (PNP)Br$$

$$\rightarrow {}^{l}(PNP)^{trans}[Mo(Br)_2pc^{2-}] + OPPh_3$$
(1)

Interestingly, the reaction of $[Mo(N)(Br)_xpc^{2-}]$ with fused PPh₃ also produces ${}^{l}(PNP)^{trans}[Mo(Br)_2pc^{2-}]$, even without the addition of (PNP)Br. While the O atom transfer to PPh₃, producing stable triphenylphosphine oxide, is the obvious driving force of the former reaction (eq. (1)), formation of the stable PNP cation seems to be that of the N atom transfer to PPh₃. The synthesis, summarized in a simplified overall picture in eq (2), has not yet been elucidated in detail, but it seems to follow closely that of (PNP)Br (eq (3)).

$$PPh_3 + Br_2PPh_3 + [Mo(N)pc^{2-}] \rightarrow (Ph_3PNPPh_3)[Mo(Br)_2pc^{2-}]$$
(2)

$$PPh_3 + Br_2PPh_3 + NH_2OH \rightarrow (Ph_3PNPPh_3)Br + HBr + H_2O$$
(3)

Accordingly, as a possible alternative, PPh₃ is supposed to react in part with the bromine species present to form dibromotriphenylphosphine, Br_2PPh_3 . Reaction of this active species with the nitrido ligand affords in a first step a phosphine iminato complex, $[Mo(NPPh_3)pc^{2-}]$, whose thermal decomposition followed by a reaction of the intermediates with PPh₃ and bromide, respectively, yields

¹(PNP)^{trans}[Mo(Br)₂pc²⁻]. The complex salt is soluble in most common organic solvents. The temperature independent (300 > T > 100 K) magnetic moment $\mu_{eff} = 3.84 \,\mu_{B}$ corresponds to the spin only value expected for Mo^{III}.

Crystal Structure of ${}^{l}(\text{PNP}){}^{trans}[\text{Mo}(\text{Br})_2\text{pc}{}^2\text{-}]$. ${}^{l}(\text{PNP}){}^{trans}[\text{Mo}(\text{Br})_2\text{pc}{}^2\text{-}]$ crystallizes triclinic (Tab. 1). The molecular structure of ${}^{trans}[\text{Mo}(\text{Br})_2\text{pc}{}^2\text{-}]^-$ is shown in Fig. 1 with the labelling scheme for the unique atoms. Mo^{III} ion is located on an inversion centre which relates the halves of the complex anion. Mo^{III} is hexa-coordinated by the four pyrrolic N atoms (N_p: N1, N3) and the two bromide ions in a *trans*-arrangement. The Mo-N_p and Mo-Br distance is 2.043(10) and 2.588(1) Å, respectively. Both distances



Fig. 1 Molecular structure of $t^{rans}[Mo(Br)_2pc^{2-}]^-$ [25]. H atoms omitted for clarity

are smaller than the corresponding sum of the ionic radii accounting for significant covalent bonding. Mo^{III} is in a trans-arrangement although the ionic radius of Mo^{III} ($r_{Mo}^{III} = 0.69$ Å [15]) is close to the borderline for *cis*-coordination ($r_M \approx 0.72$ Å). Structural data for unique chemical classes of distances and angles in the $Mopc^{2-}$ core are deposited [28]. These data are in good agreement to usual structural values [16]. The pc²⁻ ligand is not planar but in a waving conformation with the largest perpendicular displacement from the "best" N_p plane of 0.4 Å for C5 and C13, C14. Although the PNP cation is in a linear conformation $(\measuredangle (P-N-P) = 180.0^{\circ})$ and the overall geometry [28] is very similar to typical structural data, the P-N distance of 1.596(3) Å is surprisingly longer than in many other $^{l}(PNP)$ cations (1.55 Å) [17]. It is even slightly longer than in the bent conformation (1.58 Å), probably due to crystal packing effects. The structural properties agree with the IR spectrum. The strong band at 1406 cm⁻¹, assigned to the antisymmetric P-N stretching vibration $(v_{as}(P-N))$, is diagnostic for the linear conformation of the PNP cation. v_{as} (Mo-Br) is observed at 218 cm⁻¹.

Electrochemical Properties. Due to the good solubility of ${}^{l}(PNP)^{trans}[Mo(Br)_2pc^{2-}]$ it has been possible to investigate the electrochemical behaviour of a soluble Mo phthalocyaninate by standard differential-pulse (dp) voltammetry and cyclic voltammetry for the first time. Four quasi-reversible one-electron-transfer processes are observed between -1.50 and 1.30 V vs Ag/ AgCl in both voltammograms. The more sensitive dpvoltammogram is shown in Fig. 2. These data contrast significantly to most literature data based on the almost insoluble oxophthalocyaninatomolybdates [12 d]. The half-wave potential at -1.14 V is assigned to the pc ligand directed reduction with redox couple $[Mo(Br)_2pc^{2-}]^{2-}/[Mo(Br)_2pc^{3-}]^{3-}$, while that at -0.50 V corresponds to the metal directed reduction with redox couple $[Mo(Br)_2pc^2]^{-}/[Mo(Br)_2pc^2]^{2-}$. The composition and conformation of the complex anion apparently remain essentially unchanged, at least during the metal directed reduction process. This is corroborated by spectral monitoring of the reversible



Fig. 2 Differential pulse voltammogram of ¹(PNP)^{trans}[Mo(Br)₂pc²⁻] in 0.1 M (ⁿBu₄N)ClO₄/CH₂Cl₂.



Fig. 3 (a) Spectral changes accompanying the reduction of a solution of ^{trans}[Mo(Br)₂pc²⁻]⁻ in CH₂Cl₂ by (ⁿBu₄N)[BH₄] at 293 K. (b) Absorption spectrum of initial ^{trans}[Mo(Br)₂pc²⁻]⁻ in CH₂Cl₂. (c) Absorption spectrum of final ^{trans}[Mo(Br)₂pc²⁻]²⁻ in CH₂Cl₂. (d) Absorption spectrum of [(Mopc²⁻)₂] in a KBr pellet

chemical reduction of ^{trans} $[Mo(Br)_2pc^{2-}]^-$ with $[BH_4]^$ shown in Fig. 3 a. A solution of ^{trans} $[Mo(Br)_2pc^{2-}]^-$ in dichloromethane, containing a small excess of $(^{n}Bu_4N)Br$, is almost completely reduced by $[BH_4]^-$. The presence of clear and sharp isosbestic points in the spectra is consistent with a two-component system. It is only in the final stage of the reduction that the clean nature of the reaction is disturbed by precipitation of not yet characterized species. Reduction is accompanied by a colour change from blue to purple. The spectra of the pure starting and final complex in Fig. 3 b and c are very similar, but all bands in the spectrum of the reduced species are shifted to higher energy with respect to those of the precursor. These hypsochromic shifts are diagnostic for a metal centred reduction, yielding $t^{rans}[Mo(Br)_2pc^{2-}]^{2-}$. Further comparison with the spectrum of di(phthalocyanina-to(2–)molybdenum(II)), $[(Mopc^{2-})_2]$, displayed in Fig. 3 d, gives strong evidence that no dimerisation occurs during reduction. Hence, it is important to realize that formation of a dimer with a multiple Mo–Mo metal bond may easily be frustrated by reduction at low temperature. Characterization of this very interesting monomeric Mo^{II} species is in progress and will be detailed in a forthcoming paper.

Two anodic peaks are located at 0.63 and 1.27 V. As no chemical oxidation of the pc ligand has been detected so far, the process at 0.63 V is considered to account for the first metal directed oxidation with redox couple $t^{rans}[Mo(Br)_2pc^{2-}]^{-/trans}[Mo(Br)_2pc^{2-}]$. Chemical oxidation of dichloromethane solutions of $[Mo(O)pc^{2-}]$ with bromine results in a reversible Mo oxidation, probably forming $[Mo(O)(Br)pc^{2-}]$. Spectral monitoring substantiates this metal centred one electron oxidation [12 d]. It is thus suggested that the process at 1.27 V is due to the redox couple $Mo^{IV}/$ Mo^{V} with yet unknown axial ligand coordination. Finally, the shoulder at 1.20 V, not occurring in the cyclic voltammogram, is assumed to be due to the Br⁻/Br couple.

Absorption Spectra. Absorption spectra of ${}^{l}(PNP)^{trans}[Mo(Br)_{2}pc^{2-}](a, b)$

(ⁿBu₄N)^{trans}[Cr(Br)₂pc²⁻] (c) and (ⁿBu₄N)[Lipc²⁻] (d) are compared in Fig. 4. Spectra (b-c) are obtained from a solution of the relevant complex in dichloromethane, while spectrum (a) is from solid ^{*l*}(PNP)^{trans}[Mo(Br)₂pc²⁻], finely dispersed in a KBr pellet. Spectra (a) and (b) are essentially identical. The solution spectrum (b) is shifted hypsochromically as compared to spectrum (b) of the solid complex, but the shift $\Delta_{s\to 1}$ of most of the bands in the lower energy region is less than $\Delta_{s\to 1} \approx 500 \text{ cm}^{-1}$ most generally observed. Only $\Delta_{s\to 1}$ of the strong broad band at 15420 cm⁻¹ in spectrum (a) is close to the value expected.

Despite its simplicity, Gouterman's four-orbital model provides a good description of the low energy spectral data of closed-shell metal phthalocyaninates(2–) [19]. The applicability of this theoretical framework, initially developed for the description of the absorption spectra of main group porphyrinate complexes, has been confirmed by ZINDO calculations for the electronic spectrum of [Mgpc^{2–}], performed by *Cory* et al. [20]. Analogous calculations for [Znpc^{2–}] have been published recently [21]. A rough notation of the main regions of electronic absorption



Fig. 4 Absorption spectra of (a) ${}^{l}(PNP)^{trans}[Mo(Br)_2pc^{2-}]$ in a KBr pellet, (b) ${}^{trans}[Mo(Br)_2pc^{2-}]^-$ in CH₂Cl₂, (c) ${}^{trans}[Cr(Br)_2pc^{2-}]^-$ in CH₂Cl₂, (d) [Lipc^{2-}]^- in CH₂Cl₂

is indicated at the bottom of Fig. 4. Closed-shell metal phthalocyaninates show typical "D_{4h} spectra" as exemplified by the spectrum of [Lipc²⁻]⁻ shown in includes an intense "B" Fig. 4 d. It region $(a_{1u}(\pi) \rightarrow e_{\sigma}(\pi^*); \log \varepsilon \sim 5.0 \pm 0.4)$ near 15000 cm⁻¹, followed by a characteristic series of vibronic components. At higher energy the broad "Q" region of medium intensity is observed. Very often, this region is more or less split into two superimposed compo- Q_1 $(a_{2u}(\pi) \rightarrow e_g(\pi^*)) < Q_2$ nents, assigned as $(b_{1u}(\pi) \rightarrow e_s(\pi^*))$. Finally, the "Q" region is followed by the weak and broad "N" region at $\sim 37500 \text{ cm}^{-1}$. At higher energy, however, as a result of extensive configurational mixing between overlapping π , π^* and charge transfer (CT) states a clean distinction into one-electron states is of restricted value.

The spectrum of $t^{rans}[Cr(Br)_2pc^{2-}]^-$, displayed in Fig. 4c, gives an example for spectra of phthalocyaninate complexes of paramagnetic metal ions. The dominance of the three fundamental "B", "Q" and "N" regions persists. The shape of the "B" region is still comparable to that of [Lipc²⁻]⁻, but the "Q" region is definitely more intricate. To a minimum, four superimposed "Q" bands are identified at 23310, 26920, 29100

and 31510 cm^{-1} , indicating that the theoretical model for the description of the "Q" region, predicting just two excitations, is apparently insufficient. Interestingly, a comparable contour of the "Q" (and "N") region is observed for the Mo^{III} complex in Fig. 4 a and b. Therefore, a seriously more profound consideration of configuration interactions and mixing with higher energetic charge transfer states is obviously necessary to overcome this dilemma. Moreover, two intriguing additional band groups of considerable intensity start at 8260 and 20270 cm⁻¹, respectively, which have not been observed in spectra of closed-shell metal phthalocyaninates(2-). The assignment of these bands is of considerable debate. Lever et al. [5] have attempted to correlate similar band energies of a sulfonated Cr^{III} phthalocyaninate(2-) complex with the halve-wave potentials of the pc²⁻ ligand and Cr^{III} ion. Although most of the necessary redox couples have not been observed, these authors predict a " $p \rightarrow MCT(I)$ " at 7900 cm⁻¹ followed by vibronic components and a " $p \rightarrow MCT(II)$ " at 20800 cm^{-1} . Only a weak extra-band at 10960 cm^{-1} has been assigned to a TM. On the other hand, recent prominent low temperature emission spectra of a series of diacidophthalocyaninato(2–)chromates(III) give strong evidence that all three extra-band groups are TM in origin [7]. Previously, a quite similar assignment has been proposed for Cr^{III} porphyrinates by Gouterman et al. [22]. A qualitative coupling scheme of the spin-spin interactions of the lowest pc^{2-} ligand singlet and triplet (S = 0, 1) with multiplicities of Cr^{III} (S = 1/2, 3/2) is shown in Fig. 5 a. Accordingly, four spin-allowed transitions are expected up to about 25000 cm⁻¹, which have been assigned for the Cr^{III} complex as follows: ${}^4\phi_0 \rightarrow {}^4\phi_{II}$ (8260 cm⁻¹; 'trip-quartet(1)' transition: TQ1) $< {}^{4}\phi_{0} \rightarrow {}^{4}\phi_{II}$ (11330 c (14650 cm⁻¹; 'sing-quartet') $(11330 \text{ cm}^{-1};$ $TQ2 < {}^4\phi_0 \rightarrow {}^4\phi_I$ "B" or transition: SQ $< {}^{4}\phi_{0} \rightarrow {}^{4}\phi_{II}^{II}$ (20270 cm⁻¹; TQ3) [7]. Finally, a low temperature emission band at 7460 cm⁻¹ (not shown in Fig. 4) is attributed to a 'trip-sextet' transition $(^{\circ}\phi_{II} \rightarrow {}^{4}\phi_{0}; TS)$ arising from the $\hat{S} = 1 \text{ pc}^{2-}$ state coupling to the S = 3/2 state of Cr^{III} .



Fig. 5 Qualitative scheme of electronic transitions arising from spin-spin coupling of singlet and triplet "B" pc^{2-} ligand states with multiplicities of (a) Cr^{III} and (b) Mo^{III}

The spectrum of ^{trans}[Mo(Br)₂pc²]⁻ in dichloromethane, shown in Fig. 4 b, differs significantly from that of the corresponding Cr^{III} phthalocyaninate(2–). Especially the "B" region is split into three well-resolved bands of comparable intensity. As a consequence, the quite familiar dominance of the "B" region is lost, and all four regions are of comparable intensity. This is particularly found for the isolated band group at 7140 cm⁻¹, whose intensity (log ε = 4.17) is surprisingly high, much higher than that of the corresponding Cr^{III} complex (log ε = 3.5 [7]). According to the qualitative spin-spin coupling scheme for Mo^{III} in Fig. 5 b, this band is assigned to TM1. That this lowest transition is TM in origin is also supported by the luminescence spectrum of solid

(PNP)^{trans}[Mo(Br)₂pc²⁻], presented in Fig. 6 c, which shows a strong emission at 6690 cm⁻¹ obtained by excitation with 1064 nm at T < 50 K. We assign this emission to spin-forbidden TS. The energy gap between TM1 (7000 cm⁻¹; Fig. 6 a) and TS is 310 cm⁻¹, thus confirming the assumption that the sublevel spacing should be comparable to kT [22, 23]. Quite similar Stoke shifts of 520 and 430 cm⁻¹ have been reported for Cr^{1II} porphyrinates [22]. The shoulder at 6775 cm⁻¹, whose intensity is significantly higher at higher temperatures, is probably caused by the spin-allowed emission ${}^{4}\phi_{II} \rightarrow {}^{4}\phi_{0}$. Apart from some marked extrabands, another very notable feature of the TM1 region, shown in Fig. 7 a, is its striking similarity to TM1 of the Cr^{III} complex (b) and to the "B" region of the



Fig. 6 (a) Absorption spectrum of ${}^{l}(PNP)^{trans}[Mo(Br)_2pc^{2-}]$ in a KBr pellet at 293 K. (b, c) Emission spectrum of ${}^{l}(PNP)^{trans}[Mo(Br)_2pc^{2-}]$ obtained by excitation with 1064 nm at 293 K (b) and 20 K (c)



Fig. 7 Comparison of the vibronic structure of TM1 of $t^{trans}[M(Br)_2pc^{2-}]^-$ (M = Mo (a), Cr (b)) with "B" of $t^{trans}[M(Br)_2pc^{2-}]^-$ (M = Mo (c), Cr (d)) and [Lipc^{2-}]^-; extrabands are indicated

 Cr^{III} (c) and Li complex (d). Hence, the shape of the TM1 region originating from a triplet ligand state and that of the "B" region originating from a singlet ligand state is essentially identical, giving additional strong support for the correct assignment as TM. Each region typically consists of five distinct bands, denoted $v_a \cdots v_e$. The most intense band (v_a) corresponds to the 0–0 phonon line which is followed by not resolved vibronic components with averaged higher energies of ~700 (v_b), 1560 (v_c), 2320 (v_d) and 2860 cm⁻¹ (v_c). The comparatively high intensity and energy of v_c of TM1 of the Cr^{III} complex (1710 cm⁻¹; Fig. 7 b) signals some interactions with TM2.

A largely stronger mixing of the aforementioned four spin-allowed states (indicated by up-arrows in Fig. 5 b) within the TM/"B" region of the Mo^{III} complex is the most likely reason for the strong intensity transfer from the "B" transition to the three spin-allowed "trip-quartet" transitions TQ1–3. This is substantiated by an almost identical integrated absorbance between 6000 and 22000 cm⁻¹ for the Mo^{III} and Cr^{III} complex. Nevertheless, differentiation of the three transitions within the "B" region still appears to be reasonable. On account of its shape, energy and shift $\Delta_{s \rightarrow 1} = 430$ cm⁻¹ we assign the band at 15850 cm⁻¹ to SQ (former "B"). The assignment of

TQ2 at 16890 cm⁻¹ and TQ3 at 18700 cm⁻¹ follows similar arguments, especially $\Delta_{s \rightarrow 1} \approx 150$ cm⁻¹ being very similar for TQ1-3. In comparison with the corresponding Cr^{III} phthalocyaninate the averaged shift of TQ1 and TQ3 of the Mo^{III} complex is approximately 1350 cm^{-1} to lower energy, while that of TQ2 is 5660 cm^{-1} to higher energy, thus levelling the energies of SQ, TQ2 and TQ3 and favouring strong mixing of these three states of same multiplicity. Reasons for these remarkably different shifts and strong mixing may be the significantly larger spin-orbit coupling of Mo^{III} ($\xi_{Mo} = 834 \text{ cm}^{-1}$ [24]) as compared to that of Cr^{III} ($\xi_{Cr} = 254 \text{ cm}^{-1}$ [24]) and the longer effective ionic radius of Mo^{III} (r_{Mo} ^{III} = 0,69 Å $\gg r_{Cr}$ ^{III} = 0,615 Å [15]). This, in turn, amounts the covalency drastically and only a supermolecule description will be appropriate. The weak bands around 20100 cm⁻¹ are probably due to vibronic components of TO3 or to a formally spin-forbidden trip-doublet. The weak bands around 14380 cm⁻¹, also present in the spectrum of the Mo^{II} complex shown in Fig. 3c, probably indicate the presence of small quantities (<5%) of very intense H_2pc^{2-} .

Experimental Section

All reagents were commercially available and purified by standard procedures. Oxophthalocyaninatomolybdenum(IV), [Mo(O)pc²⁻] was prepared by the reaction of ammonium heptamolybdate tetrahydrate with phthalodinitrile (260 °C, 0.5 h) following the methods described in the literature [12 a]. The product was contaminated with nitridophthalocyaninatomolybdenum(V), [Mo(N)pc²⁻] (MIR: ν (Mo-N) = 1030 cm⁻¹). Oxobromophthalocyaninatomolybdenum(V), [M(O)(Br)_xpc²⁻] (x ≈ 2) was obtained by oxidation of [Mo(O)pc²⁻] with excess bromine [12 d, e].

l-Bis(triphenylphosphine)iminium *trans*-Dibromophthalocyaninato(2-)molybdate(III), ^{*l*}(PNP)^{*trans*}[Mo(Br)₂pc²⁻].

[Mo(O)(Br)_xpc²⁻] (0.8 g) was heated (280 °C, 2 h) with triphenylphosphine (2.6 g) and bis(triphenylphosphine)iminiumbromide, (PNP)Br (1.2 g) under argon. The cold melt was washed thoroughly with dichloromethane, and the purple crystalline residue dried in vacuum. Anal. for C₆₈H₄₆Br₂MoN₉P₂: Br (calcd) 12.25, (found) 12.19%. The magnetic moment μ_{eff} was 3.84 μ_{B} at 300 K and 100 K. Crystals suitable for X-ray structure determination were obtained by controlled cooling of a melt of $l(PNP)^{trans}[Mo(Br)_2pc^{2-}]$ in PPh₃.

Instrumentation

Differential-pulse voltammetry and cyclic voltammetry with scan rates of 50 mVs⁻¹ were carried out at 293 K with a Polarecord 626, Metrohm. A three-electrode system was used with a Pt button working electrode, a Pt wire counterelectrode and a Ag/AgCl(LiCl/C₂H₅OH) reference electrode. The solution of ¹(PNP)^{trans}[Mo(Br)₂pc²⁻] (~10⁻⁴ M) in CH₂Cl₂/0.1 M (ⁿBu₄N)ClO₄ was deoxygenated by passing a stream of solvent saturated N₂ for 15 min prior to recording voltammograms. The ferrocene/ferrocenium couple at 0.50 V

formula	C68H46Br2MoN9P2	fw	1306.87
crystal system	triclinic	space group	P1 (No. 2)
a (Å)	10.506(1)	α (deg)	76.186(1)
b (Å)	12.436(2)	β (deg)	67.890(1)
c (Å)	12.918(2)	γ (deg)	68.689(1)
volume $(Å^3)$	1446.5(4)	Z	1
$d_x (g/cm^3)$	1.500	$\mu ({\rm mm}^{-1})$	1.715
no. reflcns	5317	no. indep	5016
		reflcns	
R [I > $2\sigma(I)$]	R1 = 0.0782	R (all reflcns)	R1 = 0.2059

Table 2 Atomic fractional coordinates $(\cdot 10^4)$ and equivalent isotropic displacement parameters $(A^2 \cdot 10^3)$ for ${}^{l}(PNP)^{trans}[Mo(Br)_2pc^{2-}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	у	Z	U _{eq}
Мо	5000	5000	5000	24(1)
Br	4383(1)	5589(1)	6964(1)	33(1)
N(1)	7103(11)	4893(8)	4542(8)	29(2)
N(2)	6841(10)	6868(8)	3588(7)	26(2)
N(3)	4397(9)	6724(7)	4352(7)	20(2)
N(4)	1803(10)	7177(8)	4780(8)	26(2)
C(1)	7645(12)	5784(10)	3921(9)	23(2)
C(2)	5385(11)	7296(10)	3762(9)	23(2)
C(3)	4568(13)	8474(9)	3345(9)	27(3)
C(4)	5004(14)	9406(10)	2711(9)	30(3)
C(5)	3930(15)	10433(11)	2468(11)	39(3)
C(6)	2510(16)	10522(11)	2798(12)	45(4)
C(7)	1995(13)	9616(10)	3446(10)	33(3)
C(8)	3117(13)	8563(9)	3691(9)	27(3)
C(9)	2997(12)	7451(9)	4349(9)	22(2)
C(10)	1711(11)	6126(9)	5327(9)	22(2)
C(11)	357(12)	5871(10)	5872(9)	27(3)
C(12)	-1062(13)	6562(10)	5973(10)	31(3)
C(13)	-2161(14)	6060(12)	6556(11)	42(3)
C(14)	-1732(12)	4863(11)	6996(11)	38(3)
C(15)	-273(12)	4170(11)	6884(9)	30(3)
C(16)	805(13)	4674(9)	6300(9)	27(3)
P(1)	1086(3)	8906(3)	9354(2)	24(1)
N(4)	0	10000	10000	41(4)
C(17)	199(13)	7915(10)	9465(10)	30(3)
C(18)	-812(13)	7711(12)	10488(10)	36(3)
C(19)	-1549(15)	6957(12)	10610(11)	44(4)
C(20)	-1224(15)	6351(12)	9733(10)	41(3)
C(21)	-215(15)	6531(12)	8712(11)	44(4)
C(22)	530(14)	7296(11)	8565(10)	38(3)
C(23)	1824(14)	9366(10)	7888(9)	29(3)
C(24)	3227(14)	8693(10)	7247(10)	35(3)
C(25)	3754(15)	9066(13)	6118(10)	41(3)
C(26)	2868(16)	10099(12)	5670(10)	42(4)
C(27)	1519(16)	10762(12)	6300(11)	44(3)
C(28)	939(14)	10395(10)	7437(10)	33(3)
C(29)	2586(12)	8129(10)	9919(9)	27(3)
C(30)	3109(15)	6903(11)	10159(11)	44(3)
C(31)	4194(16)	6385(13)	10658(13)	57(4)
C(32)	4750(16)	7060(16)	10924(11)	55(4)
C(33)	4266(15)	8268(14)	10689(12)	51(4)
C(34)	3149(17)	8794(12)	10193(12)	51(4)

 $(CH_2Cl_2/(0.1 \text{ M} (^n\text{Bu}_4\text{N})\text{ClO}_4)$ was used as a reference potential. *Magnetic susceptibilities*: Faraday method, BSU-20, Bruker; 300–100 K. *UV-VIS-NIR spectra*: Cary 05 spectrometer, Varian; KBr pellet and CH_2Cl_2 solution. *MIR spectra*: FTIR interferometer Genesis, Mattson ATI; KBr pellet. *FIR spectra*: FTIR interferometer CS66, Bruker; polyethylene pellet. *Luminescence spectra*: FTIR interferometer CS66 with FRA 106, Bruker; neat polycrystalline probe, cryodyne cold cell with variable temperature 300–20 K, excitation with NdYAG Laser (1064 nm, 10 mW).

X-ray Structure Determination: Diffraction data of l (PNP)^{*irans*}[Mo(Br)₂pc²⁻] (crystal size: 0.3×0.3×0.5 mm³) were collected on a CAD-4 diffractometer, Enraf-Nonius, equipped with graphite-monochromated Mo-K α radiation (0.71069 Å) and a cooling device operating at 200 K. Cell parameters and an orientation matrix were determined from the least-square fit of 25 accurately centred reflections. Intensity data were collected in ω -2 θ scan mode in the range $2.2 < \theta < 25.45^{\circ}$. Data were corrected for background, polarisation and Lorentz factor. Heavy atoms were located by use of direct methods [26]. Atoms not located from the initial structure solution were found by successive difference Fourier maps with iterative cycles of full matrix least-squares refinement on F² [27]. All non-hydrogen atoms were treated anisotropically. In the final refinements hydrogen atoms were placed at idealized calculated distances of 0.93 Å with isotropic thermal parameter. Selected crystallographic and refinement data are given in Table 1 and atomic fractional coordinates and equivalent isotropic displacement parameters in Table 2. All data are deposited as supporting information [28].

This work was supported in part by the MPI für Physik komplexer Systeme, Dresden.

Literature

- Phthalocyanines, Properties and Applications, Vol 1-4, C. C. Leznoff, A. B. P. Lever (Eds.), VCH Verlagsgesellschaft mbh, Weinheim 1989–1996.
- [2] M. J. Stillman, T. Nyokong, in [1], 1989, 1, 133.
- [3] (a) A. Treibs, Liebigs Ann. Chem. 1969, 728, 115;
 (b) A. Antipas, J. W. Buchler, M. Gouterman,
 P. D. Smith, J. Am. Chem. Soc. 1978, 100, 3015;
 (c) J. W. Buchler, W. Kokisch, P. D. Smith, Struct. Bonding [Berlin] 1978, 34, 79.
- [4] M. G. Cory, M. C. Zerner, Chem. Rev. 1991, 91, 813.
- [5] A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswamy, K. Magnell, J. Am. Chem. Soc. 1981, 103, 6800.
- [6] (a) J. A. Elvidge, A. B. P. Lever, J. Chem. Soc. 1961, 1257; (b) S. Sievertsen, Dissertation, Univ. Kiel (1997).
- [7] (a) S. Sievertsen, H. Grunewald, H. Homborg, Z. Anorg. Allg. Chem. 1996, 622, 1573; (b) S. Sievertsen, B. Aßmann, H. Homborg, Z. Anorg. Allg. Chem. 1996, 622, 1685.
- [8] (a) S. Sievertsen, B. Moubaraki, K. S. Murray, H. Homborg, Z. Anorg. Allg. Chem. 1993, 620, 682; (b) S. Sievertsen, H. Grunewald, H. Homborg, Z. 1993. 1729; Anorg. Allg. Chem. 619, (c) B. E. Williamson, T. C. VanCott, M. E. Boyle, G. C. Misener, M. J. Stillman, P. N. Schatz, J. Am. Chem. Soc. 1992, 114, 2412.

- [9] (a) A. B. P. Lever, J. P. Wilshire, S. K. Quan, J. Am. Chem. Soc. 1979, 107, 3668; (b) A. B. P. Lever, J. P. Wilshire, S. K. Quan, Inorg. Chem. 1981, 20, 761.
- [10] (a) A. B. P. Lever, J. P. Wilshire, Can. J. Chem. 1976, 54, 2514; (b) A. B. P. Lever, J. P. Wilshire, Inorg. Chem. 1978, 17, 1145; (c) M. Tahiri, P. Doppelt, J. Fischer, R. Weiss, Inorg. Chim. Acta 1986, 127, L1; (d) A. Kienast, L. Galich, K. S. Murray, B. Moubaraki, G. Lazarev, J. D. Cashion, H. Homborg, J. Porph. Phthalocy. 1997, 1, 141.
- [11] (a) W. Kalz, H. Homborg, Z. Naturforsch. 1983, 38 b, 470; (b) W. Kalz, H. Homborg, H. Küppers, B. J. Kennedy, K. S. Murray, Z. Naturforsch. 1984, 39 b, 1478; (c) B. J. Kennedy, K. S. Murray, P. R. Zwack, H. Homborg, W. Kalz, Inorg. Chem. 1986, 25, 2539.
- [12] (a) H. A. O. Hill, M. M. Norgett, J. Chem. Soc. (A), 1976, 1476; (b) V. Börschel, J. Strähle, Z. Naturforsch. 1984, 39b, 1664; (c) S. J. Edmondson, P. C. H. Mitchell, Polyhedron, 1986, 5, 315; (d) T. Nyokong, Inorg. Chim. Acta, 1989, 160, 235; (e) T. Nyokong, Polyhedron, 1994, 13, 215; (f) G. Ferraudi, T. Nyokong, M. Feliz, M. Perkovic, D. P. Rillema, Inorg. Chim. Acta, 1994, 215, 27.
- [13] M. I. Federov, V. A. Shorin, L. M. Federov, *Izv. Vyssh. Uchebn. Zaved. Fiz.* 1978, 21, 158.
- [14] (a) M. Safarpour Haghighi, M. Rath, H. W. Rotter, H. Homborg, Z. Anorg. Allg. Chem. 1993, 619, 1887;
 (b) G. Ostendorp, H. W. Rotter, H. Homborg, Z. Anorg. Allg. Chem. 1996, 622, 235.
- [15] R. D. Shannon, Acta Crystallogr. 1976, A 32, 751.
- [16] B. Aßmann, H. Homborg, Z. Anorg. Allg. Chem. 1996, 622, 766.
- [17] B. Aßmann, A. Franken, H. Homborg, Z. Anorg. Allg. Chem. 1995, 621, 1715.
- [18] M. Gorsch, Dissertation, Univ. Kiel (1997).
- [19] A. J. McHugh, M. Gouterman, C. Weiss, *Theor. Chim.* Acta 1972, 24, 346.
- [20] M. G. Cory, H. Hirose, M. C. Zerner, *Inorg. Chem.* 1995, 34, 2969.
- [21] J. Mack, M. J. Stillman, Inorg. Chem. 1997, 36, 413.
- [22] M. Gouterman, L. K. Hanson, G.-E. Khalil, W. R. Leenstra, J. W. Buchler, J. Chem. Phys. 1975, 62, 2342.
- [23] (a) R. W. Harrigan, G. D. Hager, G. A. Crosby, *Chem. Phys. Lett.* **1973**, *21*, 487; (b) R. W. Harrigan, G. A. Crosby, J. Chem. Phys. **1973**, 59, 3468.
- [24] J. Bendix, M. Brorson, C. E. Schäffer, *Inorg. Chem.* 1993, 32, 2838.
- [25] G. Bergerhoff, K. Brandenburg, DIAMOND, Univ. Bonn, 1996.
- [26] A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, Univ. of Bari; M. C. Burla and G. Polidori, Univ. of Perugia; M. Camalli, Inst. Strutt. Chimica CNR, Rome, Italy; SIR92, Semi-Invariants Representation Package, 1992.
- [27] G. M. Sheldrick, Univ. of Göttingen, Germany; SHELXL93, Program for Crystal Structural Determination, 1993.
- [28] Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-407166, the names of the authors and the journal citation.