in Figure 8 is attributed to adsorption. It is of interest to note that also this wave is smaller after isomerization.

Registry No. $NiL_1(ClO_4)_2$, 57456-82-3; $NiL_2(ClO_4)_2$, 57427-14-2; $NiL_3(ClO_4)_2$, 57456-81-2; $NiL_4(ClO_4)_2$, 57427-09-5; NiL_1^+, 93984-20-4; NiL_2^+, 59461-43-7; NiL_3^+, 94061-35-5; NiL_4^+, 84026-55-1; $NiL_3(H_2O)_2^{2+}$, 93923-56-9; $NiL_4(H_2O)_2^{2+}$, 93984-21-5; $Co(NH_3)_6^{3+}$, 14695-95-5; $Ru(NH_3)_6^{3+}$, 18943-33-4; N_2O, 10024-97-2; $CO_2^{-}\cdot$, 85540-96-1; $(CH_3)_3COH$, 75-65-0; H_2O, 7732-18-5; H_2, 1333-74-0; O_2, 7782-44-7.

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Preparation and Absorption and Emission Spectra of *cis*-Bis(2-hydroxy-6-methylpyridinato)bis(triethylphosphine)dichlorodimolybdenum(II)

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The quadruply bonded dimer *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ was prepared by the reaction of a stoichiometric amount of $SiCl(CH_3)_3$ with $Mo_2(mhp)_4$ in the presence of the phosphine. The compound crystallized in a triclinic cell (space group $P\bar{1}$) with cell constants $a = 9.953$ (1) Å, $b = 11.149$ (1) Å, $c = 15.602$ (2) Å, $\alpha = 92.35$ (1)°, $\beta = 93.45$ (1)°, $\gamma = 115.51$ (1)°, and $Z = 2$. Six transitions were observed in the solution spectrum, and the lowest energy band at 540 nm was assigned as $\delta \rightarrow \delta^*$. At 5 K, the 0–0 transition and seven vibronic origins were observed. All the progressions observed were based on the Mo–Mo stretching frequency, which was 370 (12) cm^{-1} in the excited state. Strong fluorescence at 600 nm was observed from the $\delta^* \rightarrow \delta$ transition. The quantum yield was a function of wavelength varying from 0.24 at 540 nm to 0.09 at 305 nm. The fluorescence lifetime was 33.8 ns.

Introduction

Over the past several years there has been an extensive study of the electronic spectroscopy of the quadruply bonded dimers.[1,2] These systems have been of interest because their bond orders are unusual and also because their spectra are very amenable to study by a variety of techniques. The absorption spectroscopy of the molybdenum dimers has been thoroughly examined, and the lowest energy transition has been assigned as $\delta \rightarrow \delta^*$. Of late, there has been much interest in the emission spectra of these dimers because there has been some question as to the assignment. In studies on $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ it was found that the 0–0 transitions of the absorption and emission bands did not overlap.[3] This was attributed to a change in the excited-state geometry from the rigorously eclipsed geometry found in the ground state to a staggered conformation. It was later found that this change in geometry did not occur in $Mo_2Cl_4(PBu_3)_4$ because of the bulky phosphines.[4,5] In this case, the 0–0 bands nearly coincided. These studies have been pursued further and applied to a series of dimers of the form $Mo_2Cl_4(PR_3)_4$ (R = Me, Et, Pr, Bu).[6] In all cases, the 0–0 bands are identical for the absorption and emission. However, the lifetime quantum yield and band shape are dependent on the halide and the R group of the phosphine.

So far, the only dimers to have their photochemistry fully studied have not had bridging ligands. The emission spectra of $Mo_2(mhp)_4$ and $Mo_2(chp)_4$ (mhp = 2-hydroxy-6-methylpyridine anion; chp = 2-hydroxy-6-chloropyridine anion) in inert matrices have been reported.[7] However, no lifetime or quantum yields were given. In this paper, the synthesis, crystal structure, and absorption and emission spectra are reported for *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$. In addition, the lifetime and quantum yields have been determined and are the first data for a bridged quadruply bonded dimer.

Experimental Section

Preparation of *cis*-$Mo_2(mhp)_2Cl_2(PEt_2)_2$. Typically 1.0 g (1.6 mmol) of $Mo_2(mhp)_4$ prepared by the standard method[8] was refluxed in 50 mL of THF with 0.348 g (3.2 mmol) of chlorotrimethylsilane and 0.40 g (3.4 mmol) of triethylphosphine for 3–4 h. The resulting dark red solution was evaporated to dryness, and the residue was chromatographed twice on activated silica gel, with cyclohexane as the solvent. The isolated yield was 60%. The resulting *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ is bright red and is soluble in nearly all organic solvents. The solid appears to be indefinitely stable in air while solutions decompose only slowly. This same dimer can be prepared by the reaction of $Mo_2Cl_4(PEt_3)_4$ with mhp in the presence of NEt_2H.

Spectroscopy. The solution spectrum was recorded on a Beckman Model 26 UV–visible spectrophotometer and manually digitalized. The single-crystal spectrum was recorded on a Cary 17-D spectrophotometer interfaced by Varian Instruments to an Apple Computer. Two Ealing Optics Glan-Thompson prism polarizers were used, one located behind the sample and one in the reference beam. A Janis Super-Varitemp cryostat was used for the low-temperature studies. Deconvolution of the spectra was done by the method of damped least squares.[9] Mass spectra were recorded on a Vacuum Generators ZAB-2F double-focusing spectrometer. Emission spectra were recorded on a Spex Fluorolog 2 fluorescence spectrophotometer. All solution studies were done with cyclohexane as the solvent. Excitation spectra were corrected for wavelength dependence with use of a Rhodamine B quantum counter. Spectra were obtained at 77 K by immersing a quartz sample tube into a partially silvered quartz dewar filled with liquid nitrogen. Spectra were obtained as methylcyclohexane glasses. A Photochemical Research Associates fluorescence lifetime instrument was used to determine the lifetime. The excitation source was a nitrogen flash lamp operated at 380.5 nm.

Crystallography. Crystals of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ were obtained by evaporation of acetone solutions. The crystal used was a kite shaped plate with dimensions 0.30 × 0.18 × 0.05 mm. The large, well-developed face was the (001) face. The crystal was mounted on a glass fiber with epoxy cement. Indexing and data collection were done by using an Enraf-Nonius CAD-4 automatic diffractometer. The cell constants determined from the least-squares fit of 25 reflections with $24° < 2\theta < 35°$ were $a = 9.953$ (1) Å, $b = 11.149$ (1) Å, $c = 15.602$ (2) Å, $\alpha = 92.35$ (1)°, $\beta = 93.45$ (1)°, $\gamma = 115.51$ (1)°, and $V = 1555$ Å^3. For the formula $Mo_2Cl_2P_2O_2N_2C_{24}H_{42}$ the calculated molecular weight is 715.32 and for $Z = 2$ the calculated density is 1.53 g/cm^3. Data were collected at 22 °C by using the θ–2θ scan technique and graphite-monochromated Mo Kα radiation. The details of data collection and structure refinement have been reported previously.[10] Of the 4062 unique data collected, only the 3098 data with $I \geq 3\sigma(I)$ were used in the structure refinement. The absorption coefficient was 10.9 cm^{-1} and an empirical absorption correction was applied.[11]

Refinement was begun and ultimately converged in the space group $P\bar{1}$. The positions of the molybdenum atoms were determined from a

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Table I. Positional Parameters for the Atoms of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$[a]

atom	x	y	z
Mo(1)	0.34132 (8)	0.30535 (7)	0.26672 (5)
Mo(2)	0.25763 (8)	0.12733 (7)	0.18700 (5)
Cl(1)	0.2101 (3)	0.2895 (3)	0.3951 (1)
Cl(2)	0.3809 (3)	−0.0163 (2)	0.2175 (2)
P(1)	0.5598 (3)	0.2980 (2)	0.3572 (2)
P(2)	0.0373 (3)	−0.0299 (2)	0.2659 (2)
O(1)	0.4979 (6)	0.4144 (6)	0.1865 (4)
O(2)	0.1006 (6)	0.1678 (6)	0.1185 (4)
N(1)	0.1873 (8)	0.3655 (7)	0.1963 (5)
N(2)	0.4168 (8)	0.2305 (8)	0.0927 (4)
C(1)	0.0913 (10)	0.2783 (9)	0.1343 (5)
C(2)	−0.018 (1)	0.3071 (10)	0.0873 (6)
C(3)	−0.020 (1)	0.429 (1)	0.1073 (7)
C(4)	0.085 (1)	0.523 (1)	0.1678 (7)
C(5)	0.188 (1)	0.4903 (9)	0.2141 (6)
C(6)	0.304 (1)	0.587 (1)	0.2795 (7)
C(11)	0.508 (1)	0.3626 (9)	0.1133 (6)
C(12)	0.609 (1)	0.443 (1)	0.0567 (6)
C(13)	0.617 (1)	0.380 (1)	−0.0218 (7)
C(14)	0.524 (1)	0.244 (1)	−0.0419 (7)
C(15)	0.425 (1)	0.1715 (9)	0.0150 (6)
C(16)	0.319 (1)	0.028 (1)	−0.0041 (7)
C(111)	0.647 (1)	0.4496 (10)	0.4301 (6)
C(112)	0.696 (1)	0.576 (1)	0.3814 (7)
C(121)	0.536 (1)	0.163 (1)	0.4278 (6)
C(122)	0.457 (1)	0.168 (1)	0.5086 (8)
C(131)	0.711 (1)	0.302 (1)	0.2914 (7)
C(132)	0.864 (1)	0.337 (1)	0.3438 (8)
C(211)	−0.116 (1)	0.021 (1)	0.2636 (7)
C(212)	−0.270 (2)	−0.083 (1)	0.2892 (9)
C(221)	−0.042 (1)	−0.195 (1)	0.2064 (7)
C(222)	−0.080 (2)	−0.189 (1)	0.1100 (9)
C(231)	0.055 (1)	−0.067 (1)	0.3798 (7)
C(232)	0.134 (2)	−0.152 (1)	0.3966 (9)

[a] Estimated standard deviations in the last figure(s) are given in parentheses in this and all subsequent tables.

Patterson map. The rest of the atoms were located in subsequent difference Fourier maps. Anomalous dispersion terms were included in the scattering factor tables for molybdenum, phosphorus, and chlorine. In the final cycles only the molybdenum, chlorine, phosphorus, nitrogen, and oxygen atoms were refined anisotropically. The final discrepancy indices were $R = 0.048$ and $R_w = 0.066$. The largest peak in the final difference Fourier was 0.62 e/Å^3. Values for the final atomic coordinates are given in Table I.

Results

Synthesis and Structure. The synthesis of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ makes use of chlorotrimethylsilane to substitute a chlorine for a coordinated oxygen. This reagent has been used in the past to remove coordinated carboxylates.[12-14] The structure reported here proves that only the oxygens are involved. In the starting dimer $Mo_2(mhp)_4$, each molybdenum is bound to two nitrogens and two oxygens. There is a trans geometry around each molybdenum, resulting in an overall symmetry of D_{2d} for the dimer. In the $(mhp)_2$ dimer, each chlorine is trans to the remaining oxygen coordinated to each molybdenum. Effectively, the chlorosilane has replaced an oxygen with a chlorine.

The reaction of chlorotrimethylsilane with $Mo_2(mhp)_4$ does not produce a single product. In all cases, the reaction solution contained three compounds as determined by TLC on silica gel plates. Under the conditions given, the major product was the red *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$. However, a purple and an orange product were also present. These have been determined to be $Mo_2(mhp)Cl_3(PEt_3)_3$ and $Mo_2(mhp)_3Cl(PEt_3)$. Their synthesis, characterization, and properties will be reported in the future. Changing the solvent and/or reactant concentrations did not seem to eliminate the formation of these side products.

Table II. Bond Distances (Å) and Angles (deg) for *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$

Mo(1)-Mo(2)	2.103 (1)		
-O(1)	2.048 (6)	Mo(2)-O(2)	2.056 (6)
-N(1)	2.177 (7)	-N(2)	2.120 (7)
-Cl(1)	2.425 (2)	-Cl(2)	2.443 (2)
-P(1)	2.552 (2)	-P(2)	2.566 (2)
P(1)-C(111)	1.83 (1)	P(2)-C(211)	1.85 (1)
-C(121)	1.84 (1)	-C(221)	1.84 (1)
-C(131)	1.86 (1)	-C(231)	1.85 (1)
O(1)-C(11)	1.28 (1)	O(2)-C(1)	1.29 (1)
N(2)-C(11)	1.37 (1)	N(1)-C(1)	1.34 (1)
C(11)-C(12)	1.41 (1)	C(1)-C(2)	1.43 (1)
C(12)-C(13)	1.41 (1)	C(2)-C(3)	1.38 (1)
C(13)-C(14)	1.41 (1)	C(3)-C(4)	1.40 (1)
C(14)-C(15)	1.37 (1)	C(4)-C(5)	1.40 (1)
C(15)-N(2)	1.38 (1)	C(5)-N(1)	1.40 (1)
C(15)-C(16)	1.49 (1)	C(5)-C(6)	1.49 (1)
C(111)-C(112)	1.53 (1)	C(211)-C(212)	1.56 (2)
C(121)-C(122)	1.53 (2)	C(221)-C(222)	1.54 (2)
C(131)-C(132)	1.56 (2)	C(231)-C(232)	1.49 (2)
Mo(2)-Mo(1)-O(1)	95.0 (2)	Mo(1)-Mo(2)-O(2)	94.4 (2)
-N(1)	89.8 (2)	-N(2)	89.6 (2)
-Cl(1)	113.90 (7)	-Cl(2)	114.19 (7)
-P(1)	103.28 (6)	-P(2)	102.68 (7)
O(1)-Mo(1)-N(1)	87.1 (2)	O(2)-Mo(2)-N(2)	88.5 (2)
-Cl(1)	150.9 (2)	-Cl(2)	151.5 (2)
-P(1)	85.6 (2)	-P(2)	85.1 (2)
N(1)-Mo(1)-Cl(1)	90.2 (2)	N(2)-Mo(2)-Cl(2)	91.8 (2)
-P(1)	165.5 (2)	-P(2)	166.5 (2)
Cl(1)-Mo(1)-P(1)	90.15 (8)	Cl(2)-Mo(2)-P(2)	88.14 (9)
Mo(1)-O(1)-C(11)	120.9 (6)	Mo(2)-O(2)-C(1)	120.6 (5)
Mo(2)-N(2)-C(11)	116.2 (6)	Mo(1)-N(1)-C(1)	117.3 (5)
-C(15)	124.1 (6)	-C(5)	121.8 (6)
C(11)-N(2)-C(15)	119.7 (7)	C(1)-N(1)-C(5)	120.9 (7)
O(1)-C(11)-N(2)	118.2 (8)	O(2)-C(1)-N(1)	117.9 (8)
-C(12)	119.4 (8)	-C(2)	121.1 (8)
N(2)-C(11)-C(12)	122.4 (9)	N(1)-C(1)-C(2)	121.0 (8)
C(11)-C(12)-C(13)	117 (1)	C(1)-C(2)-C(3)	117.5 (9)
C(12)-C(13)-C(14)	120 (1)	C(2)-C(3)-C(4)	122 (1)
C(13)-C(14)-C(15)	120 (1)	C(3)-C(4)-C(5)	118 (1)
C(14)-C(15)-N(2)	120.6 (9)	C(4)-C(5)-N(1)	119.6 (9)
-C(16)	122.9 (9)	-C(6)	121.7 (9)
N(2)-C(15)-C(16)	116.5 (8)	N(1)-C(5)-C(6)	118.6 (9)
Mo(1)-P(1)-C(111)	108.5 (3)	Mo(2)-P(2)-C(211)	112.0 (3)
-C(121)	122.5 (3)	-C(221)	107.8 (4)
-C(131)	112.9 (3)	-C(231)	123.7 (4)
P(1)-C(111)-C(112)	112.0 (7)	P(2)-C(211)-C(212)	116.7 (8)
-C(121)-C(122)	113.3 (7)	-C(221)-C(222)	112.4 (8)
-C(131)-C(132)	114.9 (7)	-C(231)-C(232)	115.6 (9)

The dimer *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ has several unusual properties. First, the solutions and solid display noticeable fluorescence even under laboratory lighting. Secondly, the dimer is remarkably soluble in almost all organic solvents including alkanes. Lastly, the compound displays remarkable air stability for a molybdenum dimer. Crystals were grown from acetone solutions in air with only minimal decomposition. Dilute solutions used in studies of the emission spectrum displayed no change in intensity after as long as 6 h.

An ORTEP drawing of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ is shown in Figure 1, and a list of bond distances and angles is given in Table II. The molecule is situated on a general position in the triclinic cell and therefore contains no crystallographically imposed symmetry. However, if the ethyl groups of the phosphine are ignored, the idealized symmetry is C_2.

The bond distances in *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ can be compared with those observed in similar quadruply bonded dimers. The Mo–Mo distance of 2.103 (1) Å is intermediate to the 2.065 (1) Å observed in $Mo_2(mhp)_4$[8] and the 2.130 (1) Å found in $Mo_2Cl_4(PMe_3)_4$.[15] This distance is slightly shorter than the Mo–Mo bond length of 2.113 (1) Å in the analogous *cis*-Mo_2-

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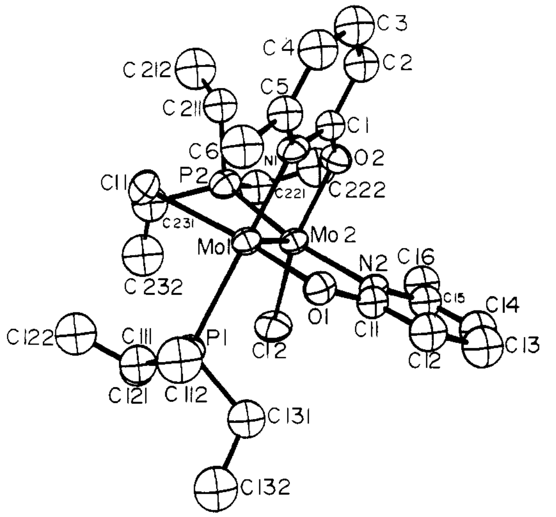

Figure 1. ORTEP drawing of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ illustrating the numbering scheme used. The ellipsoids are drawn at the 50% probability level.

$(O_2CCMe_3)_2Cl_2(PEt_3)_2$.[13] However, this is to be expected since the bond length in $Mo_2(mhp)_4$ is shorter than in $Mo_2(O_2CCMe_3)_4$.[16] Both of the Mo–O bonds in *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ are significantly shorter than the average of 2.086 (8) Å observed in $Mo_2(mhp)_4$. The situation is not as clear for the Mo–N bonds since one is shorter (at 2.120 (7) Å) and one is longer (at 2.177 (7) Å) than the 2.175 (7) Å observed for the average in $Mo_2(mhp)_4$. Similarly, there is a slight reduction in the Mo–Mo–O and Mo–Mo–N angles in the mixed-ligand dimer. On the other hand, both the Mo–Cl and Mo–P bond distances are longer by about 0.02 Å in the $(mhp)_2$ dimer as compared to those in *cis*-$Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$.[13]

Because of the problems in obtaining a pure compound, an attempt was made to sublime the solid obtained from the reaction of $Mo_2(mhp)_4$ with $Si(CH_3)_3Cl$ at 235 °C and pressures of less than 10^{-6} torr. Three bands of sublimed material were obtained in addition to large amounts of thermally decomposed material. Only a small band was fluorescent and therefore identified as *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$. The bulk of the sublimed material was in a dark brown band that occurred in the coolest part of the sublimation tube. A yellow-orange band was the third component. In order to characterize the sublimed material, the mass spectrum was studied. The most intense group of parent peaks began at *M/z* 940. Analysis of the mass pattern indicated these were the parent peaks for $Mo_4(mhp)_4Cl_4$. Similar tetramers have been obtained from the reaction of two quadruply bonded dimers and are generally brown.[12,17] The brown sublimate obtained from *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ is the corresponding tetramer. The next most intense set of parent peaks was from $Mo_2(mhp)_4$. The TLC of the material used for the mass spectroscopic study did not display the presence of any $Mo_2(mhp)_4$. Therefore, it must come from the thermal decomposition and is the yellow-orange band observed upon sublimation. Lowering the sublimation temperature did not change the products appreciably.

Spectroscopy and Photochemistry. The electronic spectrum of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ dissolved in cyclohexane is shown in Figure 2. The deconvolution suggested that it is composed of at least six transitions: 18 560 cm^{-1} (ϵ = 1520 M^{-1} cm^{-1}), 23 710 (1690), 26 160 (2630), 28 530 (1980), 31 750 (4640), 33 730 (5640). The spectrum naturally divides into three regions labeled I, II, and III in Figure 2. The only intense transition in region I is assigned to the $\delta \rightarrow \delta^*$ transition. This is in agreement with the trend observed in the electronic spectra of quadruply bonded dimers and also consistent with the polarized crystal spectrum (vide infra). The observed molar absorptivity is typical for $\delta \rightarrow \delta^*$ but is less than the values of 2100 and ~3500 M^{-1} cm^{-1} observed in $Mo_2(mhp)_4$[7] and $Mo_2(PMe_3)_4Cl_4$[15] respectively. In region III there are two overlapping bands. The fit in this region is not good. However, changing the starting values or eliminating the slope in the base line did not improve the fit. When unitary weights were used, the fit always converged to the reported values. This region can be assigned by comparison to the spectra of $Mo_2(mhp)_4$ and $Mo_2Cl_4(PR_3)_4$. In $Mo_2(mhp)_4$ there is an intense band at 35 100 cm^{-1} (ϵ = 30 000 M^{-1} cm^{-1}) which was assigned to a ligand-localized $\pi \rightarrow \pi^*$ transition.[7] This is one of the transitions in region III. An intense absorption located at about 33 000 cm^{-1} was observed in the spectra of both $Mo_2Cl_4(PMe_3)_4$[15] and $Mo_2Cl_4(PBu_3)_4$.[5] This is the second observed transition and is presumably a metal–phosphine charge-transfer band.

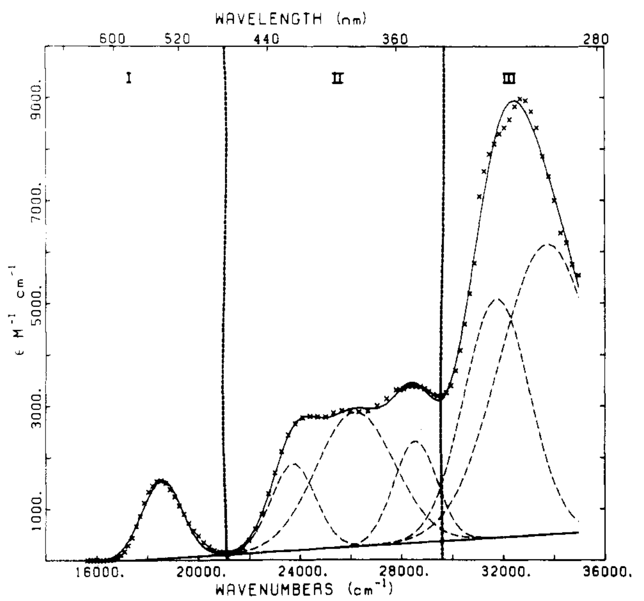

Figure 2. Electronic spectrum of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ in cyclohexane.

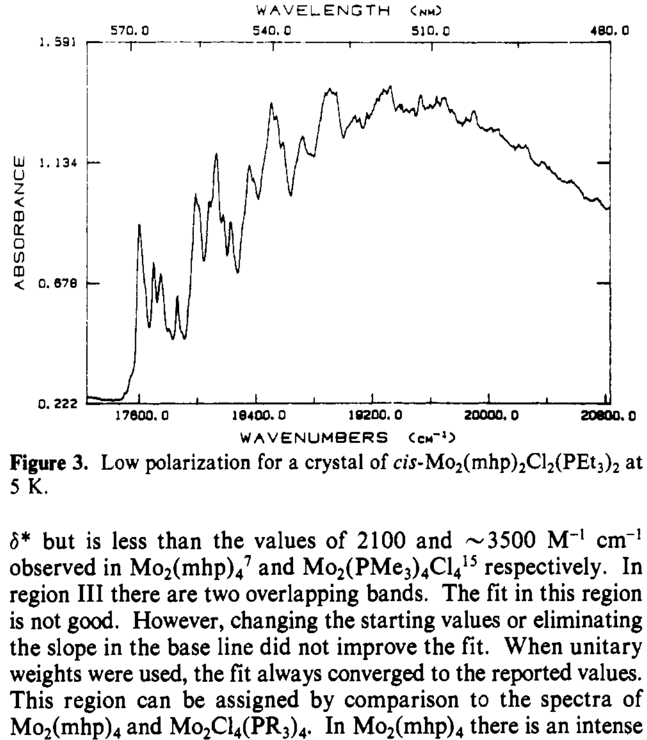

Figure 3. Low polarization for a crystal of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ at 5 K.

The three moderately intense features that compose region II of the solution spectrum are more difficult to assign. One should correspond to the β transition in $Mo_2(mhp)_4$, which occurred at 24 700 cm^{-1}.[7] This would probably be the metal–ligand charge transfer. For both $Mo_2Cl_4(PMe_3)_4$ and $Mo_2Cl_4(PBu_3)_4$ no intense transitions were observed in this range. However, a weak, unsymmetrical band was observed at ~25 000 cm^{-1} (ϵ ~ 500 M^{-1} cm^{-1}) in the trimethylphosphine dimer. Possibly two of the peaks in region II can be assigned to these same transitions. However, in the case of all the other observed transitions in *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ there has been a sizable decrease in the intensity as compared to the benchmark compounds. Therefore, it would not be expected that these bands in $Mo_2Cl_4(PMe_3)_4$ would increase

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Table III. Vibrational Fine Structure on the δ → δ* Transition for *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$

progression	λ, nm	$\tilde{\nu}$, cm^{-1}	$\tilde{\nu}_{M-M}$, cm^{-1}	comments
A_0	568.2 (3)	17 600 (10)		0–0
B_0	567.0	17 640		sh
C_0	565.2	17 690		
D_0	563.7	17 740		
E_0	561.7	17 800		
F_0	560.0	17 860		
G_0	557.3	17 940		sh
A_1	556.0	17 990	390	
B_1	555.3	18 010	370	sh
C_1	553.2	18 080	390	
D_1	551.7	18 130	390	
E_1	550.2	18 180	380	
F_1	548.1	18 220	360	
G_1	546.0	18 320	380	sh
A_2	544.8	18 360	370	
B_2	544.0	18 380	370	sh
C_2	542.0	18 450	370	sh
D_2	540.5	18 500	370	
E_2	539.4	18 540	360	
F_2	538.2	18 580	360	
A_3	534.2	18 720	360	
D_3	530.0	18 870	370	sh
E_3	529.0	18 900	360	
F_3	527.8	18 950	370	
G_3	525.8	19 020		sh
A_4	524.2	19 080	360	
B_4	523.4	19 110	. . .	
H_0	521.8	19 160		
D_4	520.0	19 230	360	
E_4	519.0	19 270	370	
F_4	517.7	19 320	370	
G_4	516.0	19 380	360	
A_5	513.5	19 470	390	
H_1	512.0	19 530	370	
E_5	509.0	19 650	380	
F_5	507.7	19 700	380	
A_6	504.0	19 840	370	
H_2	502.7	19 890	360	
E_6	499.0	20 040	390	
A_7	494.5	20 220	380	
E_7	491.0	20 370	330	
A_8	486.0	20 580	360	
E_8	482.0	20 750	380	
A_9	477.5	20 940	360	
E_9	473.5	21 120	370	
A_{10}	470	21 280	340	

av $\tilde{\nu}_{Mo-Mo} = 370 \pm 12$ cm^{-1}
av A–B = 35 ± 13 cm^{-1}
av A–C = 90 ± 12 cm^{-1}
av A–D = 144 ± 5 cm^{-1}
av A–E = 189 ± 9 cm^{-1}
av A–F = 235 ± 14 cm^{-1}
av A–G = 318 ± 21 cm^{-1}
av A–H = 1543 ± 15 cm^{-1}

[a] sh = shoulder.

in intensity in the mixed-ligand dimer. One other possibility is that a transition involving a degenerate level in D_{2h} is being split by the low C_2 symmetry in the mixed dimer. However, such a splitting would have to be greater than 2000 cm^{-1}. Since there are only two representations in C_2, there is the possibility of strong mixing of states of similar energy.

The polarized crystal spectrum at 5 K is shown in Figure 3. The crystal was ~2 μm thick. Only the low polarization is shown because the crystal was too thick to allow the other polarization to be determined accurately. Unfortunately, this was the only crystal thin enough to give a good spectrum. As the crystal was not indexed, the exact face studied cannot be determined. Complicating the problem is that three different faces (001), (010), and (0$\bar{1}$0) were prominent in the crystals indexed. However, all grew with the same basic crystal morphology making easy determination of the face impossible. In each case the direction of maximum growth was the *a* axis. This axis is nearly perpendicular to the Mo–Mo vector. For all the crystals, when observed under a polarizing microscope, the lowest absorption was always along the extinction direction closest to the *a* axis. Therefore, the lowest energy transition is *z* polarized, consistent with an assignment of δ → δ*. Because the crystal is triclinic, the extinction directions do not have to be parallel to the crystal axis. Indeed, the extinction direction closest to the *a* axis made angles of 2, 10, and 15° with this axis in the (001), (010), and (0$\bar{1}$1) faces respectively. In fact, this is the easiest way to distinguish between these faces.

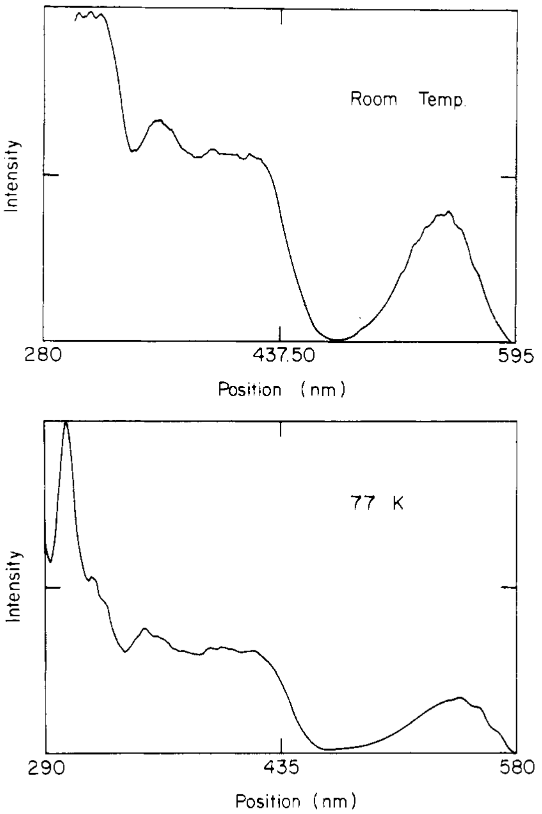

Figure 4. Excitation profile for *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ at room temperature and 77 K.

The low-temperature spectrum of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ is more characteristic of $Mo_2(mhp)_4$ and $Tc_2(hp)_4Cl$ (hp = 2-hydroxypyridine anion)[18] than of the nonbridged dimers. The 0–0 band and seven vibronic origins are observed. The vibrational structure is tabulated in Table III. All the Franck–Condon progressions are based on the symmetric metal–metal vibration, which has a mean value of 370 ± 12 cm^{-1} in the excited state. This is analogous to the values observed in the tetracarboxylate dimers and is slightly less than the 380 cm^{-1} observed in $Mo_2(mhp)_4$.[19] This is quite consistent with the reported bond distances. It is clear from the relative intensities of progressions A and E that these series are not as long as indicated. Starting at A_7 and E_7 there is a slight increase in intensity. This suggests that a second electronic transition begins on the tail end of the δ → δ* band. Thus, the original A and E series are accidentally at the same energy as the structure for this new feature. In addition, the solution spectrum fit suggests that there is a weak band on the tail end of the δ → δ*. A vibronic transition assigned to either δ → π* or π → δ* was observed in $Mo_2(O_2CCF_3)_4$ on the high-energy side of the δ → δ* transition.[20]

Because of the obvious fluorescence of *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$, a study of the emission spectrum was undertaken. The emission spectrum consisted of a single feature with maximum intensity at 600 nm. This band was the mirror image of the δ → δ* absorption band. The observed Stokes shift was only 1850 cm^{-1}, which is comparable to the 2000 cm^{-1} observed in

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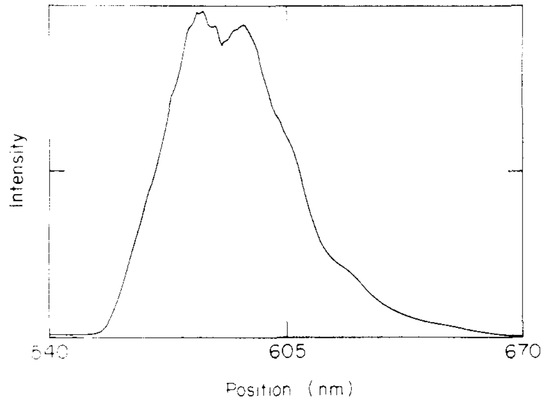

Figure 5. Emission spectrum of cis-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ at 77 K.

$Mo_2Cl_4(PBu_3)_4$.[2,3] The presence of oxygen had no effect on the emission spectrum for periods as long as 6 h. After this time, there was a slow decrease in the intensity of the emission, which correlated with a decrease in the absorption spectrum and is attributed to the decomposition of the dimer. Therefore, all studies were carried out without removal of oxygen.

The corrected excitation profiles at room temperature and 77 K are shown in Figure 4. It is obvious that the intensities in the room-temperature excitation spectrum are not in good agreement with the absorption spectrum. The absolute emission quantum yields were 0.09, 0.16, 0.17, and 0.24 for excitation at 305, 380, 420, and 540 nm, respectively. From several independent measurements, the error in the quantum yield was determined to be ±0.03. The excitation profiles measured on several different preparations were all in agreement. Also, the increase in the quantum yield with increasing wavelength agrees with the observed excitation profile. However, at 77 K the relative intensities of the excitation spectrum are in good agreement with the observed absorption spectrum. The lifetime at room temperature was 33.8 ns.

The 77 K emission spectrum is shown in Figure 5. Vibrational structure is observed. However, the spacing of 375 ± 10 cm^{-1} is inconsistent with the observed value of 370 cm^{-1} in the excited state. In fact, the separation between the two most distinct components is only 360 cm^{-1}. There are several possibilities for this apparent inconsistency. First, is the possibility of shifts in the band maxima akin to the missing mode effect.[21,22] This may be due to the difference between the single-crystal environment and that found in the methylcyclohexane glass. A contributing factor is the poor resolution in the emission spectrum. This is mainly due to the fact that the emission work was done at 77 K as compared to 5 K in the single crystal. In fact, the appearance of the 0–0 band in the crystal is very temperature dependent, as it was in $Tc_2(hp)_4Cl$.[18] Thus, the sum of the overlap of broad vibronic features may produce peaks at wavelengths different from any of the components. We are not presently able to study the fluorescence at 5 K.

Discussion

The use of chlorotrimethylsilane to replace an oxygen with a chloride has become routine. When two bridging ligands are replaced, only one partially substituted product is produced with either cis or trans geometry. However, it is not clear what factors influence the geometry of the product. When chlorotrimethylsilane was reacted with $Mo_2(O_2CCMe_3)_4$ in the presence of triethylphosphine in diethyl ether, the product was $trans$-$Mo_2(O_2CCMe_3)_2Cl_2(PEt3)_2$.[13] On the other hand, when the same reaction was done with $Mo_2(O_2CCF_3)_4$ in acetonitrile, the product was cis-$Mo_2(O_2CCF_3)_2Cl_2(NCCH_3)_2$.[14] Similarly, the reaction with $Mo_2(mhp)_4$ gave the cis product. Neither steric nor electronic factors appear to account for this reactivity pattern.

One difference in the reaction with $Mo_2(mhp)_4$ with chlorotrimethylsilane as compared with that of the carboxylate dimers is that a mixture of products is obtained and not just the stoichiometric product. Varying the reaction conditions did not appreciably change the composition of final mixture. Small quantities of the mono- and trisubstituted dimers were always produced.

The low-temperature absorption spectrum of cis-$Mo_2(mhp)_2Cl_2(PEt_3)_2$ was remarkably similar to those of $Tc_2(hp)_4Cl$[18] and $Mo_2(mhp)_4$.[19] The values for the vibrations responsible for the six vibronic origins observed in a crystal of $Mo_2(mhp)_4$[19] at 5 K are in excellent agreement with the first six origins observed in cis-$Mo_2(mhp)_2Cl_2(PEt_3)_2$. The spectrum of $Mo_2(mhp)_4$ was too intense to allow for observation 1500 cm^{-1} above the 0–0 band, and thus the seventh origin cannot be confirmed. The agreement between these two compounds is surprising because the spectra of both $trans$-$[Mo_2(O_2CCH_3)_2Cl_4]^{2-}$[23] and $trans$-$Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$[24] resembled those of the unbridged dimers in that no vibronic origins were observed. Typically, the spectra of $Mo_2(O_2CR)_4$ dimers contain at least three origins of which two are vibronic. Whether this difference between the spectra of mixed-ligand systems is because of the cis trans geometry or other factors is currently being investigated.

The most interesting aspect of this work is the intense fluorescence given off by cis-$Mo_2(mhp)_2Cl_2(PEt_3)_2$. Why this compound displays fluorescence is uncertain, but the phosphine is an essential component. When the chlorotrimethylsilane is added to $Mo_2(mhp)_4$, the color of the solution changes from yellow-orange to dark red. However, these solutions do not display fluorescence. The product in solution is presumably $Mo_2(mhp)_2Cl_2S_2$ where S is either solvent or a monodentate, N-bonded mhp. Addition, of the phosphine does not result in any appreciable change in the color but the solution immediately begins to fluoresce.

The 0–0 band in the 77 K emission spectrum is a weak feature at 17 610 cm^{-1}, which is in good agreement with the value of 17 600 cm^{-1} observed in the single crystal. The overlap of the 0–0 bands and the mirror image of the $\delta \rightarrow \delta^*$ transition in absorption with that of the fluorescence indicates that the fluorescence is $\delta^* \rightarrow \delta$.

The value of the radiative rate constant can be calculated from the quantum yield and the lifetime. If 0.24 is used for the quantum yield for excitation at 540 nm, the radiative rate constant is 7.1×10^6 s^{-1}. The rate constant calculated from the oscillator strength of the $\delta \rightarrow \delta^*$ transition (0.013) by using the standard approximations[25] gives $\sim 6.0 \times 10^6$ s^{-1}. These values are consistent with the observed radiative rate constant for $Mo_2Cl_4(PMe_3)_4$, which was 1.86×10^6 s^{-1}.[6]

The one aspect of the photochemistry of cis-$Mo_2(mhp)_2Cl(PEt_3)_2$ that is not clear is the wavelength dependence of the quantum yield at room temperature. Phosphorescence for $\delta^* \rightarrow \delta$ is not likely. The energy for this triplet–singlet transition has been calculated to be only 4800 cm^{-1} in Mo_2Cl_8,$^{4-}$ which is $\sim$ 14 000 cm^{-1} below the corresponding singlet–singlet transition. Therefore, intersystem crossing into this manifold is unlikely.[5] No other emissions other than $\delta^* \rightarrow \delta$ centered at 600 nm were ever observed in the visible region. This suggests that there are several nonradiative decay mechanisms and that there must be at least one that is available to the higher excited states, which provides a path to the ground state without going through the singlet $\delta^1\delta^{*1}$ potential well. This path may involve collision with the solvent and therefore would not be operative in a frozen glass. Another possibility is intersystem crossing into a triplet state other than $\delta^1\delta^{*1}$ followed by nonradiative decay. Whatever this process is, by 77 K it has been effectively eliminated so that all decay is

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through the $\delta^1\delta^{*1}$ state, which produces the observed fluorescence.

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Registry No. *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$, 94089-97-1; $Mo_2(mhp)_4$, 67634-80-4; Mo, 7439-98-7.

Supplementary Material Available: Listings of thermal parameters and structure factors (22 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, ERA 672, Université de Paris Sud, 91405 Orsay, France, and Department of Chemistry, University of Florence, and ISSECC, CNR, Florence, Italy

Single-Crystal EPR Study of $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$ (*t*-Bupy = 4-*tert*-Butylpyridine): Anisotropic Exchange in a Ferromagnetically Coupled Copper(II) Binuclear Complex

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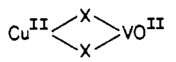
The compound $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$ is made up of binuclear copper(II) cations and noncoordinated perchlorate anions. Within the binuclear unit, the copper(II) ions are bridged by two azido groups in an end-on fashion. The magnetic behavior had shown that the metal centers were ferromagnetically coupled. This paper presents a single-crystal EPR investigation carried out at X-band frequency at 4.2 K. The principal values and the orientations of the **g** and **D** tensors associated with the triplet ground state were determined. Since two magnetically nonequivalent sites are present in the unit cell, the observed principal directions of **g** and **D** can be oriented in the molecular frame in two different ways. The solution in which one of the principal directions of **D** is as close as possible to the Cu···Cu direction is physically the most likely. **D** is composed of a dipolar contribution $\mathbf{D}^{dip}$ and an anisotropic exchange contribution $\mathbf{D}^{ex}$. This latter contribution is predominant, and its magnitude is related to the value of the two-electron-exchange integral $j^{(x^2-y^2,xy,x^2-y^2,xy)}$ involving the overlap density $\rho^{(x^2-y^2,xy)}$ between the *xy*-type orbital of an ion and the $x^2 - y^2$ type orbital of the other. A rough estimation of 150 cm^{-1} is obtained for $j^{(x^2-y^2,xy,x^2-y^2,xy)}$, leading to around 300 cm^{-1} for the $^3B_{2g}$–$^1B_{3u}$ and $^3B_{3u}$–$^1B_{2g}$ splittings within the states arising from the interaction between the $^2B_1$ (*xy*) ground state of an ion and the $^2A_1$ ($x^2 - y^2$) excited state of the other.

Introduction

The number of copper(II) binuclear complexes in which the ground state is the spin-triplet state is still very limited. Moreover in some cases where the singlet–triplet energy gap is small, the nature of the ground state is questionable. Indeed for these systems, the interpretation of both the magnetic data and the EPR spectra may be ambiguous. This arises from the fact that an intermolecular antiferromagnetic interaction may superimpose on the intramolecular ferromagnetic interaction. The zero-field splitting in the triplet state, when it is not negligible with regard to the isotropic exchange, is also a factor that makes somewhat problematic the univocal interpretation of the magnetic and EPR data. Maybe, it is why some authors recently claimed that the copper(II) binuclear complexes with a triplet ground state did not exist.[2]

In some cases, however, not only is the ground state actually the triplet but this state is largely stabilized with regard to the excited singlet. To our knowledge, up to now, three kinds of compounds exhibit such a situation:[3] (i) the planar bibridged copper(II) dimers with bridging angles close to 90°,[4–6] the ferromagnetic interaction having been interpreted in terms of accidental or quasi-accidental orthogonality of the magnetic orbitals;[7,8] (ii) the complexes with a



network,[9] the ferromagnetic interaction then arising from the strict orthogonality of the magnetic orbitals;[7,8] (iii) the end-on azido-bridged copper(II) binuclear complexes where the stabilization of the triplet state has been attributed to a spin polarization effect.[10,11] For these complexes, both the magnetic and EPR data confirm the nature of the ground state: the $\chi_M T$ (molar magnetic susceptibility × temperature) vs. T plot exhibits the characteristic plateau $\chi_M T = 2N\beta^2g^2/3k$ in the temperature range where only the triplet ground state is thermally populated; the EPR spectra at very low temperature exhibit the features characteristic of a triplet state with zero-field splitting and eventually forbidden transitions.

The EPR investigation for these complexes is far from being limited to confirming the nature of the ground state arising from the isotropic exchange. It also provides information on smaller effects such as anisotropic and eventually antisymmetric exchanges.[12–14] If the mechanism of the isotropic exchange appears today rather well understood, the situation is much less advanced for the anisotropic and antisymmetric exchanges,[8,15] and many

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