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Studies of the Emission Behavior of Quadruply Bonded Binuclear Complexes in Solution. Evidence for D_{4d} Distortions

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The sterically hindered complex $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ (Bu = *n*-butyl) is highly emissive in fluid solution (2-methylpentane) at room temperature, with $\lambda_{\text{max}}(\text{emission}) = 665 \text{ nm}$ and $\phi = 0.013$. The emission at 77 K ($\phi = 0.33$) is vibronically structured ($\Delta\nu = 340 \text{ cm}^{-1}$, corresponding to $\nu(\text{MoMo})$) and is a mirror image of the $\delta \rightarrow \delta^*$ absorption band at this temperature. Nanosecond laser flash experiments indicate the emission lifetimes to be 16 ns at room temperature and 165 ns at 77 K; the recovery of bleaching of ground-state absorption has the same lifetime, with no longer lived transients being discernible, and the magnitude of bleaching is consistent with a unit quantum yield for formation of the transient. These results are interpreted in terms of a very large splitting between the triplet and singlet $\delta\delta^*$ excited states, the emission being assigned to $\delta\delta^*$ (singlet) $\rightarrow \delta^2$. Studies of the unhindered D_{4h} complexes $\text{Re}_2\text{X}_8^{2-}$ (X = Cl, Br) in fluid solution (CH_3CN , CH_2Cl_2) reveal very weak ($\phi = 10^{-4}$ – 10^{-5}) emissions. The emission bands in these cases are broad and the emissive states are relatively long lived ($\tau = 50$ – 140 ns) at room temperature. Transient ground-state bleaching again indicates near unit quantum yields. The radiative rate constants for the $\text{Re}_2\text{X}_8^{2-}$ transients are all estimated to be $5.5 \times 10^2 \text{ s}^{-1}$. We propose that these transients possess an equilibrium geometry near D_{4d} , with the emission being assigned to $\delta\delta^*$ (singlet) (D_4 or D_{4d}) $\rightarrow {}^1A_{1g}$ (D_{4h}).

Introduction

A very recent paper from our laboratory reported² emission data for the quadruply bonded D_{4h} ions $\text{Re}_2\text{X}_8^{2-}$ (X = Cl, Br) and $\text{Mo}_2\text{Cl}_8^{4-}$ at 1.3 K. From the lack of mirror symmetry and large Stokes shifts with respect to the ${}^1A_{1g}(\delta^2) \rightarrow {}^1A_{2u}(\delta\delta^*)$ absorption bands, it was concluded that the emission could not be prompt fluorescence. The proposal was made that the emission originated from the D_{4h} $\delta\delta^*$ triplet excited state (${}^3A_{2u}$), although a geometrically distorted emissive state was also considered as a possibility. Subsequently, we prepared³ a number of phosphine-substituted neutral derivatives of $\text{Mo}_2\text{Cl}_8^{4-}$, which proved to be highly emissive in fluid solution. A detailed study of one of these derivatives, $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ (Bu = *n*-butyl), revealed properties quite distinct from the unsubstituted compounds and prompted a reinvestigation of the prototypal $\text{Re}_2\text{X}_8^{2-}$ ions in fluid solution. The results of these new studies are detailed in the present report.

Experimental Section

Solutions of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ in 2-methylpentane were prepared on a vacuum line, using Phillips "Pure" grade solvent which was freshly distilled from LiAlH_4 and subsequently transferred into the sample tube by bulb-to-bulb distillation. The solvent was then triply freeze-pump-thaw degassed, the tube sealed off under high vacuum, and the thawed solvent mixed with a sample of the molybdenum compound which had been stored and vacuum degassed in another arm of the sample tube. Less than scrupulous exclusion of air and water leads to partial or total decomposition, a soluble product being formed having a strong absorption band at 465 nm. Solutions of the $(\text{NBu}_4)_2\text{Re}_2\text{X}_8^{2-}$ complexes in spectroquality CH_3CN , CH_2Cl_2 , or a 2:1 mixture of freshly distilled 2-methyltetrahydrofuran and propionitrile, were degassed by N_2 bubbling.

Electronic absorption spectral measurements employed a Cary 17 spectrophotometer. A low-temperature absorption spectrum was obtained for a sample of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ held in thermal contact with liquid N_2 via a copper block, inside a Dewar equipped with quartz windows. Oscillator strengths of absorption bands were determined by the cut-and-weigh method.

Emission and excitation spectra were recorded on a Perkin-Elmer MPF-3A fluorescence spectrophotometer. For the determination of emission polarization ratios,⁴ polarizers were mounted on the excitation and emission slits of the spectrophotometer. For measurements of spectra at liquid N_2 temperature, an unsilvered quartz-tipped Pyrex Dewar was employed. Emission spectra in digital form were corrected for detector sensitivity using a computer program written by Dr. Kent Mann of Caltech. The true emission spectrum of the molybdenum compound could be obtained only for very dilute solutions ($< 5 \times 10^{-5}$

M) because of strong self-absorption of the emission. Emission and excitation spectra of partially decomposed solutions of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ were identical with those of pure solutions, indicating that the decomposition products neither emit nor sensitize emission of the parent compound. Excitation spectra were corrected for wavelength dependence of the source intensity using a Rhodamine B quantum counter⁵ and optically dilute (optical density less than 0.1/cm at all wavelengths) solutions.

Emission quantum yields at room temperature for the molybdenum complex were obtained using $\text{Ru}(\text{bpy})_3^{2+}$ in degassed aqueous solution as an emission standard. The emission quantum yield of the standard is constant (0.042)⁶ for exciting wavelengths $> 250 \text{ nm}$.⁷ The emission quantum yield at 77 K was obtained relative to the room-temperature emission, employing 603 nm as the excitation wavelength because the optical density of the 2-methylpentane solutions was found to be equal at this wavelength at room temperature and 77 K. In view of the large amount of data manipulation required, we only claim an accuracy of $\pm 20\%$ for emission quantum yields. Measured values were reproducible to within $\pm 5\%$.

For the Re(III) compounds, a CH_3CN solution of $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2$ ($\phi = 0.056$)⁸ was used as an emission standard. Since the low-energy tail ($\lambda > 805 \text{ nm}$) of the emission of the Re(III) compounds could not be measured with our instrument, we had to guess at the shape of this part of the band, using published data^{2,9} for solid-state emission as a guide. For this reason, and because the sensitivity of our instrument is low in the region of emission, we regard our values for these quantum yields as being reliable only to $\pm 50\%$. Relative values for the Re(III) compounds are probably accurate to $\pm 20\%$.

Flash photolysis and emission lifetimes measurements employed the N_2 laser (337-nm excitation) apparatus described in a previous publication.¹⁰

Results and Discussion

$\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$. The electronic absorption and emission spectra of this complex at room temperature in 2-methylpentane solution are shown in Figure 1. A critical review of the interpretation of the electronic spectra of quadruply bonded binuclear complexes has recently been published.¹¹ For present purposes, we note that each absorption system exhibited by $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ has an analogue in the spectrum^{12,13} of $\text{Mo}_2\text{Cl}_8^{4-}$ and that the lowest energy band, maximizing at 587 nm ($1.70 \mu\text{m}^{-1}$), is assuredly attributable to the $\delta^2 \rightarrow \delta\delta^*$ (singlet) transition.^{11,14} The corrected excitation spectrum for the emission is in excellent agreement with the absorption spectrum between 280 and 650 nm. Absolute emission quantum yields for excitation at 542, 340, and 280 nm were determined to be 0.013, 0.014, and 0.012, respectively, confirming the wavelength independence of the emission quantum

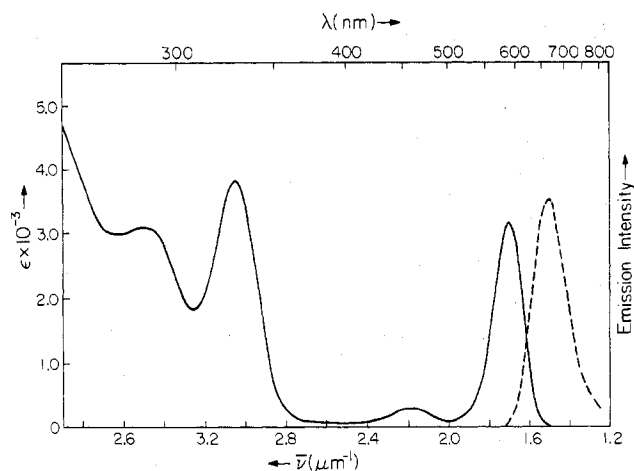


Figure 1. Absorption (—) and emission (---) spectra of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ in 2-methylpentane at room temperature ($25 \pm 2^\circ\text{C}$).

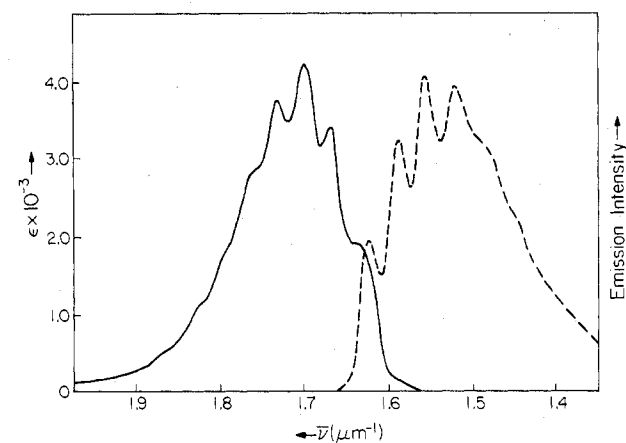


Figure 2. Absorption (—) and emission (---) spectra of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ in 2-methylpentane. The absorption spectrum was measured at 80 K and corrected for solvent contraction. The emission spectrum was measured at 77 K and corrected for detector sensitivity.

yield over this wavelength range.

The emission quantum yield was observed to increase by a factor of 24.7 for excitation at 603 nm at 77 K. Thus, the quantum yield at 77 K is ca. 0.33. The absorption and emission spectra at 77 K are shown in Figure 2. The emission polarization ratio (I_{\parallel}/I_{\perp}) at 77 K was found to be ≈ 2 for excitation at 530–580 nm. Vibronic structure was observed in both spectra, the excited- and ground-state spacings being 320 and 340 cm^{-1} , respectively, with an uncertainty of ± 10 cm^{-1} determined by the resolution. These spacings are reasonably interpreted to be the metal–metal stretching frequencies; for comparison, $\nu(\text{MoMo})$ has been reported to be 350 cm^{-1} in the ground state from Raman measurements.¹⁵

The apparent 0–0 peaks in absorption and emission occur at 1.634 and 1.621 μm^{-1} , respectively; the large overlap indicates that they represent the same transition. A weak absorption shoulder at ~ 1.59 μm^{-1} is interpreted as a hot band.

Nitrogen laser excitation at 337 nm of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ in 2-methylpentane solutions gave transient emission and absorption. The emission spectrum immediately after the laser pulse was identical with that obtained in the preceding static excitation experiments, and emission decay at all wavelengths was monotonic with a lifetime of 16 (± 2) ns at room temperature. The radiative rate constant, k_r ($=\Phi_E/\tau_E$), is calculated to be $8.5 \times 10^5 \text{ s}^{-1}$. At 77 K, the emission lifetime was found to be 165 (± 5) ns, from which we calculate $k_r = 2.0 \times 10^6 \text{ s}^{-1}$. The rate constant for fluorescence estimated from the oscillator strength (determined to be 0.026 at room

temperature and 0.027 at 77 K) employing standard approximations¹⁶ is $\sim 6 \times 10^6 \text{ s}^{-1}$.

Flash photolysis measurements yielded both transient absorption near 390 nm and bleaching of ground-state absorption. The decay of transient absorption and bleaching yielded the same lifetime at room temperature as emission decay, and no longer-lived transients were observed. From the magnitude of transient ground-state bleaching at $540 < \lambda < 570$ nm immediately after the flash, we estimate the transient quantum yield (assuming the transient to be transparent in this wavelength range and using the measured excitation pulse intensity) to be 0.90 ± 0.20 . Transient absorption due to the $\delta\delta^*$ excited state of $\text{Re}_2\text{X}_8^{2-}$ complexes has previously been assigned to $X(\pi) \rightarrow \delta$ transitions,¹⁰ and that of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ near 390 nm is probably analogous.

The 0–0 overlap of emission and absorption and the mirror-image symmetry show conclusively that the emission is attributable to $\delta\delta^*$ (singlet) $\rightarrow \delta^2$. This conclusion is strongly supported by the very high experimental radiative rate constant and by the observed emission polarization ratio. Given this, we may ask where the $\delta\delta^*$ triplet state may be, particularly since there are no longer lived transients produced by non-radiative decay of the emissive transient. There are two possible explanations.

The first possibility is that the singlet–triplet splitting is extremely small. Then, the fluorescence could be thermally activated, or a level mainly of singlet parentage might even be the lowest energy excited state. A second possibility is the other extreme, namely, that the singlet–triplet splitting is large. Then, coupling of the $\delta\delta^*$ singlet and the $\delta\delta^*$ triplet states might be sufficiently small that direct conversion to the ground state becomes the predominant nonradiative decay process; if the $\delta\delta^*$ triplet were of very low energy, it might even prove to have a shorter lifetime than the $\delta\delta^*$ singlet, owing to coupling to the δ^2 ground state.

Theoretical considerations strongly support the second possibility. The δ overlap is only of the order of 0.1.¹⁷ Thus, a weak coupling or valence bond description is appropriate. The most important feature of this coupling scheme for present considerations is that the $\delta\delta^*$ triplet is covalent, as is the δ^2 ground state, but the $\delta\delta^*$ singlet is ionic.¹⁸ One of us has proposed elsewhere¹¹ that this ionic character is responsible for the inability of SCF- $X\alpha$ -SW calculations to reproduce experimental $\delta \rightarrow \delta^*$ excitation energies.^{13,19,20} In particular, repulsion energies should be much higher for the $\delta\delta^*$ singlet, destabilizing it. It is notable that an SCF- $X\alpha$ -SW calculation for the $\delta^2\delta^*$ ion $\text{Tc}_2\text{Cl}_8^{3-}$, for which the $\delta \rightarrow \delta^*$ excitation should be less affected by electron repulsion differences between the ground and excited states, gave²¹ excellent agreement with experiment; moreover, the observed $\delta \rightarrow \delta^*$ transition energy is only 0.63 μm^{-1} , which is much lower than the observed singlet–singlet $\delta \rightarrow \delta^*$ transition energies for δ^2 ground-state molecules.¹¹

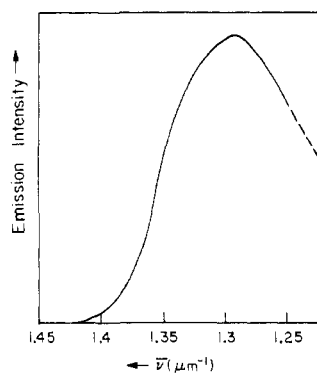
We might expect from these considerations that calculations of the $\delta^2 \rightarrow \delta\delta^*$ (triplet) excitation would be more accurate; Norman and Kolar calculated^{13b} this transition to be at 0.48 μm^{-1} for $\text{Mo}_2\text{Cl}_8^{4-}$, and their best estimate^{13b,20} places the $\delta^2 \rightarrow \delta\delta^*$ (singlet) some 0.44 μm^{-1} higher.

Thus, theoretical considerations clearly favor the interpretation in which the splitting of the Franck–Condon transitions to the singlet and triplet $\delta\delta^*$ excited states is large. Indeed, the $\delta\delta^*$ triplet may be closer to the δ^2 ground state than to the $\delta\delta^*$ singlet.

$\text{Re}_2\text{X}_8^{2-}$. Emissions from crystalline $(\text{NBu}_4)_2\text{Re}_2\text{X}_8$ compounds have previously been reported at 1.3 K² and at room temperature.⁹ We now report that emission is observable from fluid solution at room temperature. Our data are set out in Table I. The emissions are very weak; however, corrected

Table I. Emission Data for $\text{Re}_2\text{X}_8^{2-}$ Complexes in Fluid Solution ($25 \pm 2^\circ\text{C}$)

X	solvent	absorption		$10^4\phi$	τ , ns	$10^{-2}k_r$, s^{-1}
		λ_{max} , nm	emission λ_{max} , nm			
Cl	CH_3CN	682	780	0.81	140	5.7
Cl	CH_2Cl_2	686	790	0.40	75	5.3
Br	CH_2Cl_2	716	~815	0.26	50	5.0

**Figure 3.** Corrected emission spectrum of $(\text{NBu}_4)_2\text{Re}_2\text{Cl}_8$ in 2:1 2-MeTHF/EtCN at 77 K (excitation λ 620 nm).

excitation spectra for the emissions precisely match absorption spectra, indicating that impurities are not responsible.

The emission spectrum of the $\text{Re}_2\text{Cl}_8^{2-}$ salt in a 2:1 2-methyltetrahydrofuran:propionitrile glass at 77 K is shown in Figure 3. The emission quantum yield and λ_{max} at room temperature in this solvent are nearly identical with those in CH_3CN ; the quantum yield increases by a factor of 75 at 77 K. The emission polarization ratio was found to be ≈ 2.5 at 77 K. It can be seen that the emission band is very broad and structureless. The emission bands of $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Mo}_2\text{Cl}_8^{4-}$ at 1.3 K are similarly broad,² in contrast to the vibronically structured $^1\text{A}_{1g}(\delta^2) \rightarrow ^1\text{A}_{2u}(\delta\delta^*)$ absorption bands.

The 0-0 peak of the $^1\text{A}_{1g}(\delta^2) \rightarrow ^1\text{A}_{2u}(\delta\delta^*)$ absorption system in $\text{Re}_2\text{Cl}_8^{2-}$ is at ~ 710 nm ($1.41 \mu\text{m}^{-1}$); thus the Stokes shift between absorption and emission 0-0 lines is no larger than 500 cm^{-1} (Figure 3). At room temperature, the overlap between emission and absorption is quite considerable and centered at ~ 720 nm ($1.39 \mu\text{m}^{-1}$) but decreases at 77 K due to cooling out of hot bands. However, the emission maximum is not very temperature sensitive.

The lifetimes of the emissions at room temperature (Table I) proved to be identical with those of absorbing transients seen in a previous study.¹⁰ We also investigated transient bleaching of ground-state absorption at 680 nm for $\text{Re}_2\text{Cl}_8^{2-}$ in CH_3CN in the present study; the lifetime for first-order recovery is again 140 ns, with no longer-lived bleaching component, and the quantum yield for bleaching immediately after the flash is 1.0 ± 0.2 .

The radiative rate constants calculated from the data are all $\sim 5.5 \times 10^2 \text{ s}^{-1}$ (Table I). The solvent-sensitive variation of both emission quantum yield and lifetime is thus due exclusively to variation in the nonradiative decay rate. The $^1\text{A}_{1g}(\delta^2) \rightarrow ^1\text{A}_{2u}(\delta\delta^*)$ absorption bands of the $\text{Re}_2\text{X}_8^{2-}$ complexes have oscillator strengths of ~ 0.02 , from which we calculate k_r for fluorescence to be $\sim 3 \times 10^6 \text{ s}^{-1}$. Thus, these emissions are certainly not ordinary fluorescence. However, assignment to spin-forbidden emission, $^3\text{A}_{2u} \rightarrow ^1\text{A}_{1g}$, is unsatisfactory, as the polarization ratio is completely inconsistent with the theoretical value⁴ of 0.5 for $\text{E}_u(^3\text{A}_{2u}) \rightarrow ^1\text{A}_{1g}$.²²

We can present three additional arguments against a $^3\text{A}_{2u} \rightarrow ^1\text{A}_{1g}$ assignment. Firstly, we have already pointed out in the previous section that the singlet-triplet splitting should be

very large.²³ Secondly, singlet and triplet $\delta\delta^*$ states as closely spaced as experiment requires should be very strongly mixed, thereby eliminating the possibility of a strictly spin-forbidden emission transition. Yet the experimental k_r is $\sim 10^{-4}$ smaller than that calculated from the absorption band, signaling a highly forbidden transition of some sort. Thirdly, the overlap between emission and absorption is sufficiently large that, at least at room temperature, considerable thermal repopulation of the singlet from the triplet would be expected, so that deactivation processes of the singlet excited state would contribute to the lifetime and emission behavior. The long lifetime at room temperature suggests that this cannot be true; we can, however, rationalize the observed behavior if there is a considerable barrier to repopulation of the Franck-Condon $\delta \rightarrow \delta^*$ singlet excited state.

Our observations can be accounted for if the emissive transient of the $\text{Re}_2\text{X}_8^{2-}$ complexes is a singlet of noneclipsed (D_4 or D_{4d}) geometry. Emission of the type $\delta\delta^*$ (singlet) (D_4 or D_{4d}) $\rightarrow ^1\text{A}_{1g}$ (D_{4h}) is forbidden, and the resultant band system should be very broad because of very poor Franck-Condon overlap. Of particular importance is that the completely different behavior of $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$ is readily interpreted. The bulky alkylphosphine ligands of this compound should result in a large barrier to rotation about the metal-metal bond,²⁴ and the excited states must then necessarily be geometrically similar to the ground state.

It is reasonable to expect that the X-M-M bond angle in a D_4 or D_{4d} $\delta\delta^*$ singlet state will be much closer to 90° than it is in the $^1\text{A}_{1g}$ (D_{4h}) structure. As a result, the axial positions of the complex should be more open to interaction with solvent.²⁵ Such interaction may account for the longer $\text{Re}_2\text{Cl}_8^{2-}$ transient lifetime in the ligating solvent CH_3CN , which we ascribed to outer-sphere solvation in our earlier publication.¹⁰ The interaction must be weak, as there are only very small shifts of the emission and transient absorption¹⁰ spectra between CH_3CN and CH_2Cl_2 . However, even very weak axial solvation would provide an added energetic barrier toward resumption of D_{4h} geometry, in keeping with the observed decrease in the nonradiative decay rate in CH_3CN . Moreover, solvation might account for the apparent barrier to thermal repopulation of the $^1\text{A}_{2u}$ (D_{4h}) excited state.

We also noted in our earlier study¹⁰ that quenching of the transient by O_2 was inefficient. If the transient is greatly distorted geometrically from the ground state, then energy transfer must be "nonvertical", and this is known to result in slow quenching rates.²⁶ Thus the accumulated evidence makes sense if the $\text{Re}_2\text{X}_8^{2-}$ emissive transients possess a noneclipsed structure. Needless to say, elucidation of the finer details of the potential surfaces of the $\delta\delta^*$ singlet states of the $\text{Re}_2\text{X}_8^{2-}$ complexes will require much additional study.

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Registry No. $\text{Mo}_2\text{Cl}_4(\text{PBu}_3)_4$, 39306-31-5; $\text{Re}_2\text{Cl}_8^{2-}$, 19584-24-8; $\text{Re}_2\text{Br}_8^{2-}$, 19584-25-9.

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- (23) In fact, very recent ab initio calculations of the lowest electronic excited states of $Re_2Cl_8^{2-}$ place ${}^3A_{2g}$ only 0.35 eV ($0.28 \mu m^{-1}$) above the ground state (P. J. Hay, *J. Am. Chem. Soc.*, **100**, 2897 (1978)). Our interpretation of the emission data is entirely consistent with Hay's calculation.
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Magnetic Resonance Spectra of Some Mixed-Metal Paramagnetic Dinuclear Complexes with 2-Pyridyl Methyl Ketazine

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2-Pyridyl methyl ketazine (PMK) is known to form dinuclear octahedral complexes of formula $M_2(PMK)_3Y_4 \cdot nH_2O$ ($M = Co, Ni, Cu, Zn$; $Y = ClO_4, I, BF_4$). The exchange coupling between the two metal ions appears to be small. We have prepared also solid compounds containing metal complexes of formula $MM'(PMK)_3(NO_3)_4 \cdot 3H_2O$ and have recorded the proton magnetic resonance spectra of all the complexes. The isotropic shifts of the ligand protons have been discussed in terms of a simple additive model according to which they are the result of two independent contributions, one from the closer and the other from the farther metal ion. This model allowed us also to assign all the observed signals in the mixed-metal species. Dipolar contributions to the isotropic shifts have been discussed using ESR data. The effect of the two neighboring paramagnetic centers on the signal widths is discussed.

Introduction

Although the published papers regarding dinuclear transition-metal complexes are extremely numerous,¹⁻⁶ there are few reports on compounds which contain two different metal ions.⁷⁻¹¹ An investigation of this type of compound should in principle provide new experimental data which help in working out an exhaustive theory of magnetic interactions in polynuclear metal complexes. Further they can be used as models for understanding the mechanism of action of naturally occurring substances which contain couples of different metal ions.¹²

Magnetic resonance spectroscopy is in principle a powerful tool in investigating the nature of metal-metal interactions, since it can provide information on the effect of a metal ion on both the energetics and the relaxation properties of the neighboring metal ion. In particular nuclear magnetic resonance can provide information on the role of the ligands in the superexchange pathway as well as on the electronic states of the coupled metal centers,^{13,14} while electron spin resonance can yield information on the spin state of the complex and provide parameters which help in the interpretation of the NMR experiments.

The simplest dinuclear systems to study were those where exchange interactions are small; therefore we considered the complexes formed by the tetradentate ligand 2-pyridyl methyl ketazine (PMK). This ligand is known¹⁵ to form paramagnetic nickel(II) and cobalt(II) complexes of general formula $M_2(PMK)_3Y_4 \cdot nH_2O$ ($Y = I, ClO_4, BF_4$; $n = 2, 3$), which have

been postulated to contain dinuclear $M_2(PMK)_3^{4+}$ cations, where each metal ion is in a pseudooctahedral environment. We have also synthesized the copper(II) and zinc(II) homologue derivatives and solid compounds containing the mixed metal complexes $MM'(PMK)_3^{4+}$. We wish to report here their magnetic resonance spectra.

Experimental Section

Synthesis of the Complexes. The ligand 2-pyridyl methyl ketazine (PMK) was synthesized and purified according to the reported procedure.¹⁵ Cobalt(II), copper(II), and zinc(II) nitrate derivatives of general formula $M_2(PMK)_3(NO_3)_4 \cdot 3H_2O$ were prepared by mixing methanolic solutions containing stoichiometric amounts of the metal salt and of the ligand at room temperature. Crystals began to appear after a few minutes; they were filtered, washed with methanol, and dried in vacuo. The nickel(II) homologue was prepared by addition of a stoichiometric amount of the nickel(II) salt to a stirred suspension of the ligand in water. After 30 min the unreacted ligand was removed by filtration and acetone was added until crystallization occurred. The brown complex was filtered, washed with acetone, and dried in vacuo.

The compounds of analytical formula $M_{2-x}M'_x(PMK)_3(NO_3)_4 \cdot 3H_2O$, which are believed to contain the heteronuclear "mixed" species $MM'(PMK)_3^{4+}$, in addition to the homonuclear species $M_2(PMK)_3^{4+}$ or $M'_2(PMK)_3^{4+}$, were prepared using the procedure followed for the nickel(II) derivatives, i.e., by addition of aqueous solutions containing two metal salts in various molar ratios to suspensions of the stoichiometric amount of the ligand in water. Crystals were formed by addition of acetone. All these complexes are very soluble in water and therefore can be conveniently used for 1H NMR studies. The perchlorate and iodide derivatives (those of copper(II) and zinc(II)