

Table I. ^{33}S NMR Data^a

compd	solvent	δ , ppm ^b	ω , Hz
(Et ₄ N) ₂ [MoS ₄]	MeCN	373	45
(NH ₄) ₂ [MoS ₄]	H ₂ O	344	38
(Pr ⁿ ₄ N) ₂ [(CN)CuS ₂ MoS ₂]	MeCN	445	257
(Pr ⁿ ₄ N) ₂ [(PhS)CuS ₂ MoS ₂]	MeCN	436	383
(Pr ⁿ ₄ N) ₂ [(CN)AgS ₂ MoS ₂]	MeCN	257	830
(Pr ⁿ ₄ N) ₂ [(CN)CuS ₂ MoS ₂ Cu(CN)]	MeCN	139	835
(Et ₄ N) ₂ [WS ₄]	MeCN	183	24
(NH ₄) ₂ [WS ₄]	H ₂ O	159	13
(Pr ⁿ ₄ N) ₂ [(CN)CuS ₂ WS ₂]	MeCN	248	404
(Pr ⁿ ₄ N) ₂ [(CN)AgS ₂ WS ₂]	MeCN	106	974
(Pr ⁿ ₄ N) ₂ [(CN)CuS ₂ WS ₂ Cu(CN)]	MeCN	16	959

^a 40 °C; spectrometer frequency, 15.3 MHz; concentrations were 0.4 M except for that of (Et₄N)₂[MS₄] in MeCN, which was 0.1 M.
^b Referenced to 2 M aqueous Cs₂SO₄.

For fast isotropic molecular rotation,^{1b} the line width at half-height, ω , is related to the asymmetry parameter, η , the quadrupole moment, eQ , the electric field gradient at the ^{33}S nucleus, eq , and the molecular correlation time, τ , by¹

$$\pi\omega = 0.1(1 + \eta^2/3)(eQ)^2(eq)^2\tau \quad (1)$$

Observed line widths are very sensitive to the factors eq and τ .

Line widths of four-coordinate sulfur species (sulfones, sulfonic acid derivatives) are much narrower than those of two- and three-coordinate analogues (sulfides, sulfoxides, etc.), apparently a function of field gradient.^{2,3} In addition, terminal thio ligands in the simple thiomolybdates and -tungstates [MO_{4-n}S_n]²⁻ (M = Mo, W; n = 1-4) exhibit fairly narrow line widths in the range 10-400 Hz.^{5,6} This property appears to be a function of M-S π bonding reducing the effective p-electron density at the sulfur nucleus with a consequent reduction in field gradient.^{6,7}

The thiometallates act as bidentate ligands to a range of metal atom centers.⁸ Work from this laboratory has documented a linear correlation between ⁹⁵Mo and ¹⁸³W chemical shifts for the thiometallates [MO_{4-n}S_n]²⁻,⁹ and this correlation has been extended^{6,10} to ³³S and ¹⁷O chemical shifts. ⁹⁵Mo and ¹⁸³W spectra have been reported⁹ for the bi- and trinuclear complexes [(CN)M'S₂MS₂]²⁻ (M' = Cu, Ag) and [(CN)CuS₂MS₂Cu(CN)]²⁻, and the present paper details a ³³S NMR study of these species.

Experimental Section

The cyano compounds were synthesized and characterized according to ref 9, and the thiolato analogues via ref 11. MeCN was dried with P₂O₅ prior to fractional distillation.

The ³³S spectra were measured at 40 °C on solutions of concentration 0.1-0.4 M prepared in dried degassed MeCN or degassed deionized H₂O and sealed into glass sample tubes. Spectra were acquired with a JEOL FX-200 spectrometer operating at a resonance frequency of 15.3 MHz using a specially constructed horizontal solenoid coil¹² tuned to ³³S. The 90° pulse width was typically 23 μ s. The spectra were acquired using a modified ACOUSTIC¹³ sequence in order to minimize acoustic ringing effects and to reduce the dead time required. The number of transients required to obtain a good signal to noise ratio varied with concentration and line width and was in the range 10⁴-10⁶ (0.5-6 h accumulation time) in the present work.

The spectra were obtained without using a lock, and the chemical shifts are quoted relative to external 2 M cesium sulfate.¹⁴ Chemical

shifts for compounds with narrow (<400 Hz) and broad (>400 Hz) line widths are considered to be accurate to 4 and 8 ppm, respectively (Table I). See ref 14 for comments on the concentration dependence of ³³S chemical shifts.

Results and Discussion

Observed chemical shifts, line widths, and structural assignments are given in Table I. Our experimental capabilities permit observation of resonances with line widths less than 3000 Hz. Up to 10⁶ transients were required at 40 °C to achieve satisfactory signal to noise ratios (>3) in the concentration ranges available (0.1-0.4 M).

As a result of the high point symmetry (T_d) and consequent low field gradient at sulfur, a single narrow resonance is observed for [MS₄]²⁻ (M = Mo, W) (Table I) and can be assigned unequivocally to a terminal sulfur atom.^{5,6}

Line widths increase by at least an order of magnitude upon binding of [MS₄]²⁻ to M'(CN). One signal only was seen for all the binuclear and trinuclear anions examined (Table I). The known static structures^{9,11} feature a single sulfur site in [(CN)CuS₂MS₂Cu(CN)]²⁻ and, respectively, two and three inequivalent sulfur sites in [(CN)M'S₂MS₂]²⁻ and [(PhS)CuS₂MS₂]²⁻. It is possible that some of the individual resonances are too broad to be observed with the present experimental capabilities, and this would apply particularly to the PhSCu site in [(PhS)CuS₂MoS₂]²⁻.^{2,3}

However, it is also likely that rapid ligand exchange leads to a single exchange-averaged signal for the thio ligand sites. Substitution of Ag¹ for Cu¹ in both the Mo and W binuclear complexes results in a significant increase in line width. Intriguingly, the ⁹⁵Mo line widths showed the opposite behavior.⁹ The observations cannot be rationalized by differences in molecular correlation time. It is probable that exchange effects are influencing the observations.

The [MS₄]²⁻ units are acting as bidentate dithiolate ligands in the present systems. Rapid exchange is a characteristic of dithiolate ligands, especially when bound to d¹⁰ Cu¹ or Ag¹ centers.¹⁵ Unfortunately, variable-temperature studies could not be used to probe possible exchange effects as the ³³S resonances will be broadened at lower temperatures by the longer molecular correlation times.

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Registry No. [(CN)CuS₂MoS₂]²⁻, 80011-36-5; [(CN)AgS₂MoS₂]²⁻, 86430-75-3; [(CN)CuS₂WS₂]²⁻, 90790-28-6; [(CN)AgS₂WS₂]²⁻, 86430-77-5; [(CN)CuS₂MoS₂Cu(CN)]²⁻, 80642-82-6; [(CN)CuS₂WS₂Cu(CN)]²⁻, 90790-32-2.

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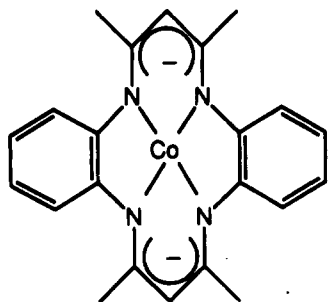
Newly Resolved ESR Spectrum of a Low-Spin Cobalt(II) Macrocylic Complex in 3-Methylpyridine

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Introduction

We have previously reported the electron spin resonance (ESR) studies of 1:1 adducts of low-spin cobalt(II) dibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecaheptaenane, CoL.¹ In an attempt



to study six-coordinated 2:1 adducts of CoL complexes, we obtained a five-coordinated cobalt(II) complex with well-resolved nitrogen superhyperfine (shf) splittings along the x - and z -directions. The shf structure along the x -direction was generally not resolved in previous studies.^{1,2} We now report the ESR studies of a newly resolved nitrogen shf structure along the x -direction of a 1:1 adduct of CoL in 3-methylpyridine.

Experimental Section

Materials. The CoL complex was prepared as previously reported and was recrystallized under an inert atmosphere as a violet solid, from acetonitrile.³ 3-Methylpyridine was purchased from Eastman, was reagent grade, and was distilled from potassium hydroxide pellets.

Sample Preparation. ESR samples were prepared under a dry atmosphere of nitrogen. The solid CoL sample (sufficient to yield ca. 0.01 M solution) was dissolved in 3-methylpyridine previously deaerated with a stream of nitrogen gas for 15 min. About 0.25 mL of this solution was transferred to a quartz ESR tube, and the sample was degassed on a vacuum line using the freeze-pump-thaw method before the tube was sealed.

Physical Measurements. ESR spectra were obtained with a Varian E-9 X-band spectrometer with Varian temperature control accessories.

Calculations. ESR spectra were simulated using the computer program previously described.¹ The line width was found to vary with orientation and m_l as previously reported.¹

Results and Discussion

Figure 1A shows the ESR spectrum of CoL in 3-methylpyridine recorded at 90 K. The spectrum consists of three groups of eight cobalt hyperfine lines indicating an interaction of the unpaired electron with a single cobalt nucleus ($I = 7/2$). The low field and the upfield regions of the spectrum show shf splittings due to interaction with one nitrogen nucleus ($N = 1$), which indicates the formation of a 1:1 adduct of CoL with 3-methylpyridine. The spectrum, in general, is similar to those observed by Schrauzer et al.⁴ for vitamin B_{12r} in aqueous solutions in the presence of various amines, where again the cobalt is expected to be bonded to one amine. The main difference between this spectrum and those reported for vitamin B_{12r} is the unusual well-resolved triplets of the cobalt hyperfine components on the x -axis of CoL in 3-methylpyridine. Upon contact with air, the 1:1 adduct reacted with oxygen and formed a six-coordinate dioxygen adduct. No differences between spectra recorded at 9 and 90 K were observed. At higher temperatures, spectra became less resolved as expected when line broadening due to spin-lattice relaxation occurs. This broadening prevented liquid solution spectra from being observed.

Figure 1B displays the best computer simulation of the ESR spectrum of CoL in 3-methylpyridine. ESR parameters for CoL in 3-methylpyridine calculated with the aid of computer simulation are $g_x = 2.470$, $g_y = 2.170$, $g_z = 2.00$, $A_x = 0.0051$, $A_y = 0.0031$, $A_z = 0.0098$, $A_x^N = 0.00127$, $A_y^N = 0.00096$, and $A_z^N = 0.00159$ cm⁻¹. The ESR parameters obtained are characteristic of d⁷ ions with an electron mainly in the d_{z²} orbital.⁵⁻⁸

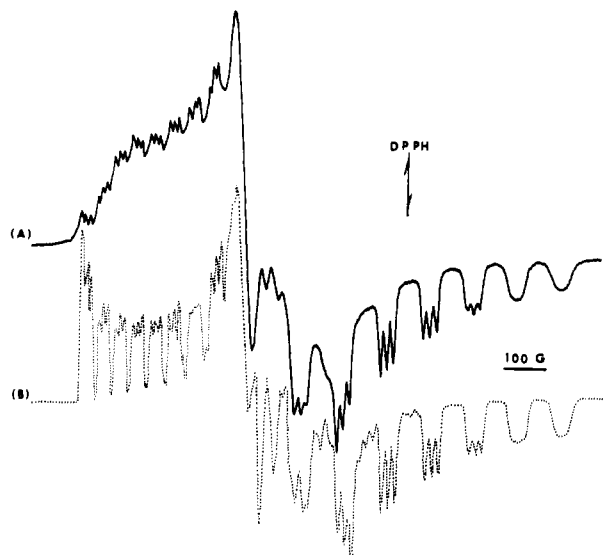


Figure 1. (A) ESR spectrum of CoL in 3-methylpyridine at 90 K. (B) Computer simulation.

McGarvey has extended the theory for the spin Hamiltonian parameters of low-spin Co(II) complexes to third order.⁹ The molecular orbital parameters calculated from the ESR parameters using this theory are $c_1 = 0.035$, $c_2 = 0.075$, $c_3 = 0.320$, $b = 0.05$, $P = 0.0123$, and $K = 0.0033$. In McGarvey's equations, $c_1 = \zeta/\Delta(^2B_1)$, $c_2 = \zeta/\Delta(^2B_2)$, $c_3 = \zeta/\Delta(^4B_1)$, $P = gg_{\pi}\beta_n(r^{-3})$, K is the Fermi contact term, and $\zeta = 515$ cm⁻¹ is the spin-orbit coupling constant of Co(II).¹⁰ The half-filled orbital in the ²A₁ ground state is $(ad_{z^2} + bd_{x^2-y^2})$; Δ^2B_1 , Δ^2B_2 , and Δ^4B_1 correspond to the energy difference between the ground state and the $(d_{x^2-y^2}, d_{yz}, d_z^2)^6d_{xz}^1$, $(d_{x^2-y^2}, d_{xz}, d_z^2)^6d_{yz}^1$, and $(d_{x^2-y^2}, d_{xz})^4d_{yz}^1, d_z^2^1, d_{xy}^1$, respectively.⁹ The energy differences Δ_{xz} and Δ_{yz} calculated from molecular orbital parameters c_1 and c_2 are 14 700 and 6900 cm⁻¹, respectively. The difference between Δ_{xz} and Δ_{yz} is due to the difference between the σ -donor and π -acceptor property of the axial ligand which leads to different interaction between the macrocyclic ligand and the cobalt 3d orbitals.

The unpaired electron densities on the cobalt ion are calculated from the nuclear hyperfine coupling constants. The values calculated for the spin density on the cobalt ion are $\rho_{3d} = 0.48$ and $\rho_{4s} = 0.06$. These values are calculated using the following equations: $\rho_{4d} = P/0.0254$ and $\rho_{4s} = (K + 0.0084 \rho_{3d})/0.1232$, respectively. The ligand hyperfine coupling constants for nitrogen are used to obtain the spin density on the coordinating axial atom. The isotropic coupling constant for N gives the 2s spin density, $\rho_{2s} = a_{iso}/a_{2s}^*$ ($a_{2s}^* = 0.0514$ cm⁻¹), while the anisotropic coupling constant yields the 2p spin density, $\rho_{2p} = A_z^N - a_{iso}^N/a_{aniso}^*$ ($a_{aniso}^* = 0.00319$ cm⁻¹).¹¹ The 2s and 2p spin densities for the nitrogen donor atom of 3-methylpyridine ligated to CoL complex are $\rho_{2s} = 0.025$ and $\rho_{2p} = 0.099$, respectively. The total nitrogen atom spin density calculated for CoL in 3-methylpyridine, $\rho_N = \rho_{2s} + \rho_{2p} = 0.124$, is greater than that calculated for Co(*p*-COOH)TPP in pyridine, 0.063.⁸ This effect is most likely due to both the distortion from planarity and shorter cobalt-nitrogen bond length in CoL than in Co(*p*-COOH)TPP which presumably corresponds to stronger interaction between the cobalt atom of CoL and the nitrogen ligand than in the case for Co(*p*-COOH)TPP.

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Time-Resolved Infrared Spectroscopy of $\text{Rh}_2(1,3\text{-diisocyanopropane})_4(\text{BPh}_4)_2$

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Binuclear d^8 complexes have been extensively studied because of their interesting bonding characteristics, spectroscopic properties, and photochemical reactions.¹ The changes in metal-metal and metal-ligand bonding upon photoexcitation are of interest in these systems. Characterization of the excited-state bond length changes may provide an understanding of the role played by the ligands in controlling the dynamics of the excited state.

In this report, we focus on the ligand-bridged complex $\text{Rh}_2\text{b}_4^{2+}$ ($\text{b} = 1,3\text{-diisocyanopropane}$). In particular, we are interested in how the Rh-Rh, Rh-C, and C≡N bonds are displaced upon photoexcitation. From a knowledge of both the ground- and excited-state vibrational frequencies associated with these bonds, their excited-state displacements may be calculated (*vide infra*). The Rh-Rh and Rh-C frequencies are known from resonance Raman studies.² However, no reliable value for the excited-state C≡N frequency is known. We now report the time-resolved IR (TRIR) spectrum of the excited state in the 2130-2200- cm^{-1} (C≡N stretching) region.

Samples were photolyzed with 750 μJ /pulse at 532 nm (with a frequency-doubled, Q-switched Nd:YAG laser operating at 10 Hz). An infrared diode laser provided probe light, which was detected by a small-element InSb detector. Calibration of the probe wavelength was accomplished by observing the spectral output of the laser in an FTIR instrument. Signals were amplified 2500 times prior to digitization with a Tektronix Model 7912 HB transient digitizer. Digitized signals were averaged and analyzed on a Mac II computer system. Each point in the transient spectrum is calculated from the maximum deflection of the transient signal. Each transient is the average of 640-1920 laser shots. Figure 1 shows an example of the high-quality transient IR data obtained, in this case at 2173 cm^{-1} . Observed lifetimes for both the bleach and transient absorbance were 6 (± 1) μs , in agreement with that found previously for the $\text{Rh}_2\text{b}_4^{2+}$ triplet excited state.⁴ The relatively large uncertainty observed for the lifetime (± 1 μs) is attributed to variable oxygen concentration in the sample cell and not to noise in the transients.

Shown in Figure 2 is the TRIR transient difference spectrum obtained for $\text{Rh}_2\text{b}_4^{2+}$.³ This spectrum is obtained point-by-point at various IR frequencies from data such as those shown in Figure 1. The spectrum shows a bleach of the ground-state absorbance at 2193 cm^{-1} and a growth in absorbance that peaks near 2177 cm^{-1} . (The peak of the excited-state absorption band is taken as the calculated peak from the double Lorentzian fit to the data. As can be seen in Figure 2, the fit to the data is quite good and also reproduces the ground-state peak at 2193 cm^{-1} .)

Transient UV/vis absorption spectroscopy has shown that the $\text{Rh}_2\text{b}_4^{2+}$ excited state has appreciable absorbance at 532 nm,⁴ and thus excitation with intense pulses at 532 nm might result in

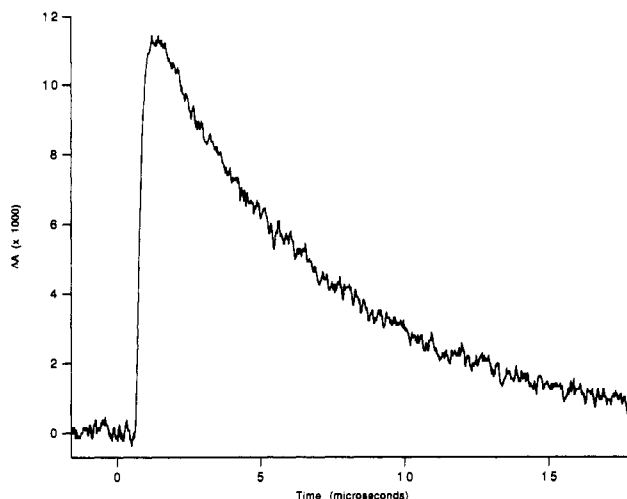


Figure 1. Transient decay for 7.9×10^{-4} M $\text{Rh}_2\text{b}_4^{2+}$ in CH_3CN , probing at 2173 cm^{-1} (average of 320 shots). Decay yields a best fit single-exponential lifetime of 6.1 μs .

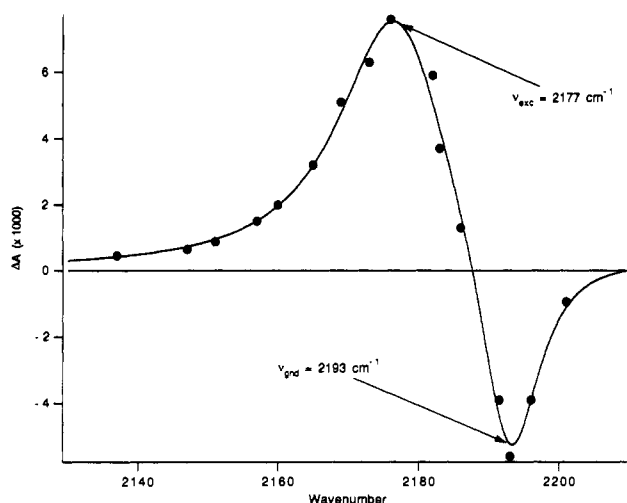


Figure 2. TRIR difference spectrum for 7.9×10^{-4} M $\text{Rh}_2\text{b}_4^{2+}$ in CH_3CN . The solid line is a calculated double-Lorentzian best fit to the data (●).

observation of multiphoton effects. We find, however, that the decrease in absorbance near the ground-state frequency displays a linear dependence on incident pulse energy. Identical behavior is observed for the increase in absorbance at 2177 cm^{-1} . Additionally, our observation of a 6- μs decay for the excited state indicates that we are observing behavior associated with the triplet state. Thus, under our experimental conditions, only the triplet state contributes to the observed TRIR spectrum.

There is one further complication that might arise: at sufficiently high concentrations, $\text{Rh}_2\text{b}_4^{2+}$ is known to form end-to-end dimers and higher oligomers.⁵ These effects, however, are not expected to be important for solutions of concentrations less than millimolar. Furthermore, the solutions used in this study (concentrations of 7.9×10^{-4} and 3.9×10^{-4} M) showed no evidence for oligomerization in their visible spectra. (Dimers of $\text{Rh}_2\text{b}_4^{2+}$ display a new absorbance band centered at 778 nm.⁵) No con-

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