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LETTER

Preparation, characterization and electron spin resonance study of a low spin Co(II) N_2S_2 complex

Robert D. Bereman*, Jay R. Dorfman

Department of Chemistry, North Carolina State University,
Raleigh, NC 27695-8201 (USA)

and Sung-Nak Choi

Department of Chemistry, Pusan National University, Pusan
609-735 (Korea)

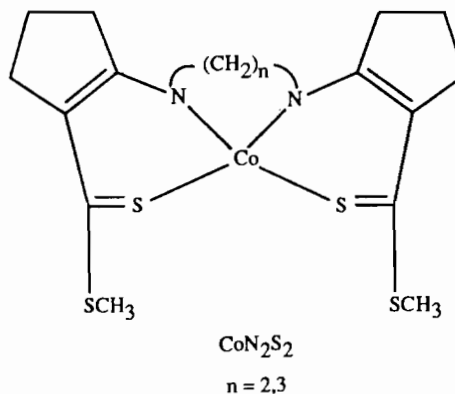
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Introduction

Low spin Co(II) complexes continue to attract considerable attention due to their ability to function as oxygen carriers [1a–d]. The vast majority of four-coordinate low spin Co(II) complexes have the ability to bind a Lewis base in an axial position to form a five-coordinate Co(II) complex which may then bind O_2 to become six-coordinate. The O_2 adducts also lend themselves amenable to ESR studies. Much work has been reported in this area and these O_2 adducts have characteristic spin Hamiltonian parameters [2]. Most of the Co(II) systems studied have been with N_2O_2 , S_4 , and particularly N_4 ligand systems, to which the porphyrin family of compounds belong. The ground state electronic configuration for these porphyrin systems which bind a Lewis base in an axial position (and then bind O_2), has generally been assigned as $(d_{xz}, d_{x^2-y^2}, d_{yz})^6(d_{z^2})^1$ based on ESR studies [3]. Much less certainty has surrounded the assignment of the ground state of the four-coordinate uncomplexed Co(II) systems. Maki *et al.* derived a series of relationships for the spin Hamiltonian parameters of Co(II) expected for each ground state [4]. Fitting the ESR parameters as best as possible to the equations then gives the most likely ground state configuration. While this approach was used by workers in this area for some time, more advanced treatments of low spin Co(II) have appeared in the literature. In particular, McGarvey's later treatment of these systems

included the possible importance of low-lying quartet states and related doublet states which can be coupled to the doublet ground state by spin-orbit perturbations [5]. In addition, the mixing of the d_{z^2} and $d_{x^2-y^2}$ orbitals in a lower symmetry was also included.

We report here the synthesis, characterization and ESR study of a low spin Co(II) N_2S_2 system using the approach of McGarvey to interpret the spin Hamiltonian parameters, and derive a reasonable choice for the ground state configuration. To our knowledge, this represents one of the few studies of a low spin Co(II) N_2S_2 system.



Experimental

The synthesis and all manipulations of this compound were carried out using standard Schlenk techniques. Methanol was degassed by successive freeze-thaw cycles.

Spectra

IR spectra were recorded with a Perkin-Elmer 521 spectrophotometer with the sample in anhydrous Nujol mulls supported on CsBr plates. Optical spectra were recorded in degassed CH_2Cl_2 on a Cary 14 spectrophotometer. ESR spectra were collected as previously described [6].

Elemental analysis

Analysis was obtained from Atlantic Microlabs, Atlanta, GA.

Synthesis: Co ($n = 2,3$)

The ligands N,N' -ethylenebis(methyl-2-amino-1-cyclopentenedithiocarboxylate) ($n = 2$) and the propylene analogue ($n = 3$) were prepared by the method of Bordas *et al.* [7]. The thermal instability of the starting material, ammonium 2-amino-1-cyclopentene dithiocarboxylate, was overcome by a later method (yield ~ 75%) [8]. The Co(II) complexes were obtained by slowly adding a methanolic solution (30 ml) of 1.0

*Author to whom correspondence should be addressed.

mmol cobalt(II) acetate tetrahydrate (Aldrich) to a solution of the ligand (1.0 mmol) dissolved in benzene (50 ml). The solvents had been degassed and the preparation was carried out under an argon atmosphere. The solution was refluxed for more than 1 h during which time crystals began to separate. After cooling to room temperature, the compounds were filtered and washed successively with benzene, methanol and water. The compounds were not recrystallized because they seemed to decompose in the solvents during this process. The yields obtained were about 30%. *Anal.* Calc. for $C_{16}H_{22}N_2S_4Co$: C, 44.75; H, 5.13; N, 6.52; S, 29.84. Found: C, 44.78; H, 5.16; N, 6.50; S, 29.87%. Calc. for $C_{17}H_{24}N_2S_4Co$: C, 46.03; H, 5.45; N, 6.32; S, 28.91. Found: C, 45.94; H, 5.38; N, 6.34; S, 28.84%.

Results and discussion

Careful study of the pertinent IR data for the $Co(n=2)$ compound (Table 1) indicates a complex degree of delocalization in the cobalt complex as compared with the free ligand. More specifically, the $\nu(C=C)$ of the ligand appears at $\approx 1575\text{ cm}^{-1}$ in the cobalt complex indicating only partial double bond character. In addition, the $\nu(C-N)$ in the ligand appears at 1250 cm^{-1} but is found at higher energies in the metal complex, at 1280 cm^{-1} , indicative of $C=N$ character. This trend has also been observed in the analogous copper and nickel compounds of this particular ligand system, and has been assessed as proof of extensive π -delocalization in these systems. The optical spectrum of $Co(n=2)$ is similar to other square-planar $Co(II)$ complexes reported [9] (Table 2). These low spin $Co(II)$ complexes are usually quite sensitive to O_2 addition and all spectra must be collected under an O_2 -free atmosphere. Three bands of d-d origin are to be expected for these complexes. In practice, however, the lowest energy band usually found at 4.0–6.0 kK is often obscured by solvent absorption in this region of the spectrum. The other two absorptions are usually found in the 9.0–11.0 and 16.0–18.0 kK ranges.

TABLE 1. IR spectral features for $Co(n=2)$ compound^a

Ligand	$Co(n=2)$	Assignments
1600(s)	1575(s)	$\nu(C=C)$
1325(m)	1310(m)	$\nu(SCH_3)$
1250(s)	1280(s)	$\nu(C-N)$
940(m)	940(m)	
905(m)	905(m)	
725(m)	725(m)	$\nu(C=S)$
	510(m)	$\nu(Co-N)$

^aUnits are cm^{-1} .

TABLE 2. Optical data for $Co(n=2)$ compound^a

Peak position (kK)	ϵ^b
10.5	40
19.2	450
21.7	5500
30.1	13000
35.6	18000

^aSolvent was degassed CH_2Cl_2 . ^bUnits of molar absorptivities are $M^{-1}\text{ cm}^{-1}$.

TABLE 3. ESR parameters for $Co(n=2)$

g_{xx}	3.047
g_{yy}	1.967
g_{zz}	1.942
$\langle g \rangle^c$	2.278
A_{xx}^a	0.00983
A_{yy}^b	0.0041
A_{zz}	0.00208
$\langle a \rangle_{Co}^c$	0.00533

^aA units are cm^{-1} . ^bEstimated from poorly resolved peaks.

^cObtained as isotropic values 300 K.

X-band ESR spectra of the $Co(n=2)$ complex were collected at 100 and 300 K (Table 3). The spectra at 100 K were obtained as a frozen glass of the compound dissolved in CH_2Cl_2 . The spectrum appears to possess nearly axial symmetry, with two of the three principal g values being less than 2.0023. As noted by other workers, because the linewidth in the high field portion of the spectrum is large, assignment of all the principal values of the g and A tensors is difficult [10]. If the largest principal value of g is assigned as g_{xx} , as has been done for similar systems, the ground state may be rationalized as either $(d_{xz}, d_{x^2-y^2}, d_{z^2})^6(d_{yz^1})$ or $(d_{xz}, d_{z^2-y^2}, d_{yz})^6(d_{z^2})^1$. The explanation for this is derived from McGarvey's relationship where the equation used for g_{xx} is greatly affected by the term describing the separation of these two states. In the vast majority of ESR studies of low spin $Co(II)$ appearing in the literature, the separation of these two states has not usually been greater than approximately 1.5 kK, thus facilitating the mixing of a higher multiplet state into the ground state.

In order to accurately determine the ground state, the orientation of the g and A tensors in the molecular framework must be known. In the absence of a single-crystal ESR study, an approximate treatment can be used. Using McGarvey's equations (all coupling constants positive), the spin Hamiltonian parameters were used to obtain the best fit to either a (d_{yz^1}) ground state or a $(d_{z^2})^1$ ground state. A fit was obtained for a d_{z^2} ground state with $g_{yy} > g_{zz}$. For this ground state, $P = 0.0080\text{ cm}^{-1}$, $K = 0.0038\text{ cm}^{-1}$ and

$C_2 \cong 0.17$, where $C_2 = \xi/\Delta(^2B_2)$, and $\Delta(^2B_2)$ is the separation between the ground and the $(d_{xz}, d_{x^2-y^2}, d_{yz})^6(d_{yz^1})$ state. Even if the y and z directions are reversed, or if contributions from quartet states are included or if some mixing of the $d_{x^2-y^2}$ orbital into the d_{z^2} ground state occurs, the ESR parameters for $\text{Co}(n=2)$ do not fit the d_{z^2} ground state any better than those presented in Table 4.

Recalculation of g_{yy} and g_{zz} using $C_2 \cong 0.17$ gives values of 1.952 and 2.950 compared to the experimental values of 1.967 and 3.047, respectively. The agreement of the two g_{yy} values is rather good and lends further support towards the proposed electronic ground state as d_{z^2} .

One other fit of the ESR parameters was obtained, although it was less acceptable than the d_{z^2} ground state (Table 4). For a d_{yz} ground state, a fit was obtained with $P = 0.0332 \text{ cm}^{-1}$, $K = -0.0049 \text{ cm}^{-1}$ and $\eta_3 \cong -0.17$, where $\eta_3 = \xi/\Delta(^2A_1)$ is the separation between the ground state and the $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ state. Of the two sets of parameters presented, the first, that of a d_{z^2} ground state is more acceptable. The low value of P for a d_{z^2} ground state is approximately 31% of the free ion value for Co^{2+} of 0.0254 cm^{-1} [11]. The large reduction of P from 0.0254 cm^{-1} may be rationalized as due to extensive metal-ligand covalency. The extended π -delocalization present in the complex as observed based on the IR assignments of $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{N})$ further supports this conclusion. Even further support for this hypothesis comes from the detailed ESR and crystal structure data for the analogous copper and nickel complexes, where considerable metal-ligand covalency has been demonstrated [12a-e]. The positive value for K , the Fermi contact term, indicates admixture of $4s$ orbital character into the d_{z^2} ground state, which is to be expected for approximate C_{2v} symmetry. The P value for the d_{yz} ground state is actually higher than the free-ion value, but this could be attributed to the approximate nature of the calculation. While some caution is required in

assigning ground states for low spin Co(II) complexes possessing low symmetries, the fit for the d_{z^2} ground state is more realistic. In addition, extended Hückel MO calculations on the analogous copper(II) complex of the ligand show that the singly-occupied HOMO contains approximately 40% $3d$ character [12c]. This also suggests that this fit for a d_{z^2} ground state is reasonable.

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TABLE 4. P and K values and coefficients used to determine ground state for $\text{Co}(n=2)$

	P (cm^{-1})	K (cm^{-1})	C_2^a	η_3^a
d_{z^2}	0.0080	0.0038	0.17	
d_{yz}	0.0332	-0.0049		-0.17

^aSee ref. 5.