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Spectroscopic and magnetic properties of square-planar bis[(cyclooctane-1,5-diyl)bis(pyrazol-1-yl)borato]cobalt(II)

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Abstract

Ligand-field spectra, EPR spectra and magnetic susceptibility of the title compound are described in terms of square-planar Co(II) in the low-spin state ($S=\frac{1}{2}$). The presence of two short, agostic, Co–H contacts (2.16 Å) results in a very slow relaxation, allowing the observation of EPR signals even at room temperature. This relaxation behaviour is also responsible for the fact that solid state NMR spectra (^{13}C and ^{1}H) could not be observed for this compound. The magnetic moment of 2.05(3) BM ($g_{av}=2.18(3)$) in the 77–300 K region, agrees with the EPR g values for the powder ($g_{\parallel}=1.65(5)$ and $g_{\perp}=2.37(5)$; $g_{av}=2.13(5)$). Dopes of the title compound in the corresponding Zn compound (not X-ray powder isomorphous with the Co compound) and the Ni compound (powder isomorphous with Co compound), on the other hand, show quite different, and beautifully resolved EPR spectra. In the Zn lattice a very sharp EPR signal, with inverted g values at $g_{\parallel}=2.05$ (with an $A_{\parallel}$ value of 18 Gauss) and $g_{\perp}=2.00$, indicating a Co^{III}–O_2^- species, appears to be present. Unfortunately, this mixed compound could not be purified through recrystallization, since on each purification step some Co(II) was lost from the lattice. In the isomorphous Ni lattice, however, the Co hyperfine splitting nicely shows up in a rhombic signal with hyperfine splittings present on each of the three g values and superhyperfine on g_z; the parameters are $g_x=2.68(2)$ ($A_x=115(5)$ G), $g_y=2.54(4)$ ($A_y=135(5)$ G) and $g_z=2.01(2)$ ($A_z=165(5)$ G; $A_N=18(1)$ G). These EPR values differ slightly from the frozen-solution data of the pure Co compound in toluene, for which the parameters $g_x=2.70$ (very broad, A_x unresolved), $g_y=2.30(2)$ ($A_y=65(5)$ G) and $g_z=2.02(2)$ ($A_z=150(5)$ G) are derived. Ligand-field spectral data of the pure Co compound are in agreement with a square-planar CoN_4 chromophore. In solutions of organic solvents, like toluene, THF and CH_2Cl_2, the colour changes somewhat and the ligand-field maxima are shifted slightly; however, no tetrahedral geometry can be deduced from these spectra, in agreement with frozen-solution EPR spectra. The ligand-field spectrum of the Co-doped zinc compound, on the other hand, shows clear bands due to tetrahedral Co(II). Solid state ^{1}H and ^{13}C NMR spectra of the pure Ni compound show almost the same spectrum as the diamagnetic Zn compound, indicating that the Ni(II) is indeed low spin in the solid state. No signals were found indicating the presence of agostic M---H interactions. On the other hand, IR spectra clearly show C----H bands indicative for agostic M----H interactions, i.e. at 2690 (Co), 2780 (Cu) and 2800 (Ni) cm^{-1}, whereas the non-isomorphous Zn compound has the C–H stretching vibration at 2820 cm^{-1}.

Introduction

The coordination chemistry of poly(pyrazol-1-yl)borate ligands is currently undergoing a renaissance after its discovery more than 25 years ago [1]. The renewed and rapidly growing interest stems from the fact that regiospecific substituents in the pyrazole rings allow control of steric factors. This has made possible the synthesis and structure of, for example, tetrahedral Ni(II) and Fe(II), activation of small molecules like dinitrogen and dioxygen, and the study of the catalytic properties of such compounds [2].

Sometime ago the X-ray structure of a very unusual Co(II) compound was described [3], which appeared to contain two very short Co----H contacts (2.16 Å). This has raised the question

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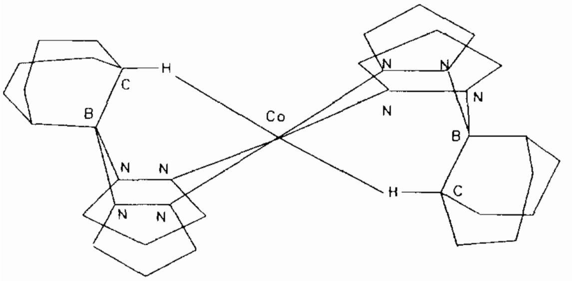

Fig. 1. Schematic structure of $[Co(LL)_2]$.

whether any unusual or special spectroscopic or magnetic effects would be imposed by the presence of these hydrogens and the unusual geometry for Co(II). This structure is schematically depicted in Fig. 1.

Therefore, we have undertaken a spectroscopic study on the solid title compound, using ligand-field, EPR, IR, NMR and magnetic susceptibility. Two related compounds with diamagnetic host lattices (i.e. the Ni(II) and Zn(II) compounds) were used to obtain magnetically diluted systems.

The results show, surprisingly, that the EPR spectra for Co(II) can already be observed at room temperature, which is unusual, even for low-spin Co(II) compounds and which is related to the unusual structure. Other spectral and magnetic data will be discussed as well and will be related to the solid state structure.

Experimental

Starting materials and synthesis

The title compound was prepared as described previously [3] and recrystallized from methylene chloride. Corresponding Zn and Ni(II) compounds, either pure or doped with a small amount of Co(II), were prepared similarly.

Ligand-field, EPR, IR, NMR, powder X-ray patterns and magnetic susceptibility

Solid state ligand-field spectra were measured in the diffuse reflectance mode on a Perkin-Elmer 330 instrument equipped with a data station (33 000–5000 cm^{-1}) fitted with a reflectance attachment using $MgSO_4$ as reference material.

Solution and solid state ^{1}H and ^{13}C NMR spectra were measured on a Bruker WM-300 spectrometer and a Bruker WM-400 instrument.

IR spectra from 4000 to 200 cm^{-1} were recorded as KBr pellets on a Perkin-Elmer 580 spectrometer. X-ray powder diagrams were obtained using the Guinier technique, applying Cu Kα radiation.

Magnetic susceptibility measurements were performed on a Faraday balance calibrated with $CoHg(SCN)_4$ in the 77–300 K region.

EPR powder spectra were recorded on a Jeol RES-J2X instrument (X-band frequencies) and on a Varian E9 (Q-band frequencies; 77 K) using standard conditions.

Results and discussion

The title compound is most unusual, mainly through its agostic hydrogen–cobalt contacts of 2.16 Å; for paramagnetic species such agostic contacts are very rare. The resulting Co(II) geometry is to be described as tetragonal, with a *trans*-CoN_4H_2 chromophore, although a square-planar description is equally possible. The ligand-field maxima in the solid state are found at 8000, 11 500, 20 200 and 23 500 (shoulder) cm^{-1}. These values are in the range for the square-planar low-spin Co(II) compounds [4]. The compound is easily dissolved in solvents like toluene, THF and CH_2Cl_2, and then a small colour change occurs, resulting in band maxima at 13 000, 17 800(sh), 20 000 and 21 200(sh) cm^{-1}, indicative of a small change in geometry.

The dope in the Zn(II) compound has band maxima at 8000 (weak, broad), 17 600 and 19 000 cm^{-1}, which agrees with a (distorted) tetrahedral CoN_4 chromophore [4].

The solid state behaviour of the compound as studied by magnetic susceptibility is as one would expect for Co(II) in a square-planar environment with one unpaired electron per cobalt(II), i.e. low spin. The values for the magnetic moment, μ_B, vary from 2.08–2.04 upon decreasing the temperature from 300–77 K, corresponding with a powder g value of 2.18(5).

Solid state and solution NMR spectra were not successful for the pure Co(II) compound, and only broad lines were observed in proton and carbon spectra (two broad resonances at 24 and 120 ppm). These broad lines apparently result from paramagnetic effects. However, the pure Ni(II) compound and the pure Zn compound (both diamagnetic), do show interesting ^{13}C solid state NMR spectra. All signals due to the pyrazole rings can be clearly distinguished near 100–140 ppm, whereas the cyclooctyl carbon signals are observed near 20–32 ppm. Unfortunately, no separate signals were found for the agostic Ni----H interactions.

The most interesting property of the title compound undoubtedly is the fact that EPR spectra can be observed at room temperature. This is unusual for Co(II), even in the low-spin state [5]. The lines, however, are quite broad and therefore also the dopes in the corresponding Zn and Ni

TABLE 1. EPR parameters of $M(LL)_2$ compounds obtained at X-band frequencies, unless indicated otherwise

Parameters	Compounds				
	$Co(LL)_2$ solid 77 K	$Co(LL)_2$ in $C_6H_5CH_3$ 77 K[a]	Co(II) in $Ni(LL)_2$		Co(II) in $Zn(LL)_2$ 77 K
			300 K	77 K Q-band	
$g_{\parallel}$ (g_z)	1.65(5)[b]	2.02	2.01	2.05	2.05
$A_{\parallel}$	u[d]	151	165[c]	150	18
g_y	u	2.30	2.54	2.43	u
A_y	u	65	135	130	u
g_x (or $g_{\perp}$)	2.37(5)	2.70(5)	2.68	2.60	2.00
A_x	u	u	115	125	u

[a] Frozen solution in toluene. [b] Accuracies in g values are ± 0.02 and in A values ± 5 Gauss, unless indicated otherwise. [c] Nitrogen superfine splitting resolved (9 lines: $A_N = 18(1)$ G) on a few $A_{\parallel}$ lines. [d] u = unresolved.

compounds had to be studied. These data are summarized in Table 1.

The EPR parameters differ for the several compounds. The signal in the doped Zn(II) compound, undoubtedly is due to a trace of a Co(III)—O_2^- species, and will not be discussed further. Upon subsequent recrystallizations, this species disappears from the lattice, resulting in a complete diamagnetic sample, i.e. without the presence of any Co(II) or Co(III), as also seen from the decolorization.

The spectrum of the Co-doped Ni(II) compound shows beautiful resolution (see Fig. 2), with all three g values showing hyperfine splittings (8 lines resulting from a Co nuclear spin of 7/2). Even nitrogen superhyperfine splittings were observed on a few g_z lines (all with 9 lines having $A_N = 18(1)$ G, corresponding to 4 N-donor atoms. A similar spectrum, though less well resolved at low magnetic field is found for a frozen toluene solution of the compound, see Table 1. Detailed analysis of such spectra is to be found in ref. 5. The differences between Q-band, X-band powder data and the frozen solution data are relatively small, and for the frozen solutions this can be interpreted as being a result of a slight change in metal-ion geometry upon dissolution.

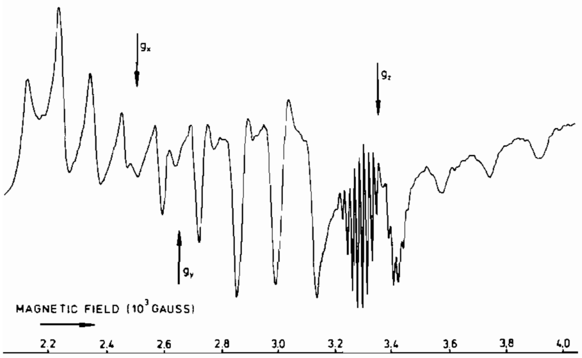

Fig. 2. EPR powder spectrum for Co(II)-doped $[Ni(LL)_2]$ at 300 K and X-band frequencies.

Conclusions

It has been shown that the spectroscopic and magnetic behaviour of the title compound, both as a pure solid state species and in inert frozen solution is quite unusual, which can be ascribed to the presence of the agostic Co----H interactions. These interactions, due to the rigid structure of the R_2 entity on boron, lead to a completely different geometry than that of $[Et_2B(pz)_2]_2Co$, which is tetrahedral, and devoid of agostic bonding, although the latter ligand does exhibit agostic interactions in other compounds [6].

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