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Short Communication

Bis(1-methylbenzotriazole)dinitratocobalt(II): A Pseudo-Octahedral Complex with Pseudo-Tetrahedral Magnetochemical and Ligand Field Characteristics

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Summary. The reaction between cobalt(II) nitrate and 1-methylbenzotriazole (*MeBTA*) leads to a complex with unusual magnetochemical and ligand field characteristics. The synthesis and the physical and spectroscopic properties of the pseudo-octahedral complex $[Co(MeBTA)_2(NO_3)_2]$ are described.

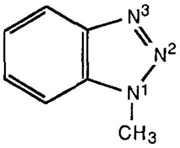
Keywords. 1-Methylbenzotriazole; Complexes of corrosion inhibitors; Ligand field spectra; Magnetic moments; Pseudo-octahedral cobalt(II) complexes.

Bis(1-methylbenzotriazol)dinitratocobalt(II): Ein pseudo-octaedrischer Komplex mit pseudo-tetraedrischen magnetochemischen und Ligandenfeld-Charakteristika (Kurze Mitt.)

Zusammenfassung. Die Reaktion zwischen Kobalt(II)nitrat und 1-Methylbenzotriazol (*MeBTA*) führt zu einem Komplex mit ungewöhnlichen magnetochemischen und Ligandenfeld-Eigenschaften. Die Synthese und die spektroskopischen Eigenschaften des pseudo-octaedrischen Komplexes $[Co(MeBTA)_2(NO_3)_2]$ werden beschrieben.

Introduction

We have initiated a systematic study of the coordination chemistry of benzotriazoles, because of the remarkable efficiency of this class of ligands as corrosion inhibitors for copper, copper alloys and a few other metals [1–6]. The reaction between $Co(NO_3)_2 \cdot 6\,H_2O$ and 1-methylbenzotriazole (*MeBTA*, I) led to a product with unusual magnetochemical and ligand field characteristics, which are described in the present communication.



I, MeBTA

Experimental

Analyses, physicochemical measurements and spectroscopic techniques were carried out by published methods [7, 8]. The complex was prepared by adding a warm solution of $Co(NO_3)_2 \cdot 6\,H_2O$ (3.0 mmol) in absolute ethanol (10 ml) to a, vigorously stirred, hot solution of *MeBTA* (6.1 mmol) in 15 ml of absolute ethanol. To the reaction mixture, 3.5 ml of triethylorthoformate were added for dehydration purposes. The resulting solution was heated gently for 1 h. The complex crystallized by the addition of ca. 20 ml of *n*-hexane to the cooled solution. The precipitate was collected by filtration, washed with ether and dried *in vacuo* over silica gel. Yield: 65%. Anal. calc. for $CoC_{14}H_{14}N_8O_6$: Co 13.12, C 37.43, H 3.15, N 24.95%. Anal. found: Co 13.31, C 37.16, H 3.21, N 25.19%.

Results and Discussion

Physical and spectral data are presented in Table 1. We could not obtain samples for single-crystal X-ray structural analysis. The complex is microcrystalline and stable in atmospheric conditions. The X-ray powder diffraction pattern indicates that Co(*MeBTA*)$_2$(NO$_3$)$_2$ is not contaminated with starting materials. Molecular weight measurements in acetone indicate that the complex is monomeric in solution. It is a non-electrolyte in this solvent and also in nitromethane [9]. The TG/DTG/DTA curves show that the complex explodes violently at ca. 260°C.

The slight shift of ν(N=N) and ν(N—N) to higher wavenumber in the IR spectrum of Co(*MeBTA*)$_2$(NO$_3$)$_2$, compared with the frequencies of these modes in the spectrum of *MeBTA*, seems to indicate that a monodentate n_1 coordination, possibly via N^3, occurs in the present complex. It is known from X-ray crystal structures of complexes containing neutral *BTAH* ligands [1, 3, 10] (*BTAH* = benzotriazole), that this ligand prefers to coordinate exclusively in a monodentate fashion via N^3; this type of coordination leads to a slight decrease of the N^1—N^2 distance, but does not influence the N^2—N^3 distance, as compared with the corresponding bond lengths in the free *BTAH* molecule [11]. The vibrational fundamentals of the nitrato groups are strongly indicative for the presence of chelated bidentate nitrates [12].

While the magnetic moment of Co(*MeBTA*)$_2$(NO$_3$)$_2$ at room temperature is in the region expected for pseudo-tetrahedral complexes [13], the d-d electronic spectrum of this complex in the solid state (Fig. 1) and in solution differs from spectra of typical pseudo-tetrahedral Co(II) complexes [12–14]. The band at ca. 19 000 cm^{-1}, although similar in general contour to the ν_3 visible band of other tetrahedral Co(II) complexes, is at a higher energy than would have been expected [14]. Moreover, the molar extinction coefficient of the visible band in solution is clearly higher than the values expected for pseudo-octahedral stereochemistry but appreciably lower than those found for pseudo-tetrahedral Co(II) complexes [13, 14]. Also the near-IR spectrum consists of two d-d bands instead of one expected for high-spin pseudo-octahedral 3d^7 systems [14]. The number and the frequencies of the d-d bands in the spectrum of Co(*MeBTA*)$_2$(NO$_3$)$_2$ let us rule out five-coordinate stereochemistries [14].

The above peculiar magnetic and spectral behaviour has been found in a very limited number of some other Co(II) complexes of the type CoL_2(NO$_3$)$_2$ (L = a phosphine or arsine oxide [15], a hindered monodentate aromatic amine [16] and 1-methyl-3,4-diphenylpyrazole [17]). This behaviour has been explained [15] by

Table 1. Physical properties, diagnostic IR bands and magnetochemical and ligand field spectral data of Co(*MeBTA*)$_2$(NO$_3$)$_2$

Color	deep red	magnetochemical data	
Λ_M(S cm^2 mol^{-1})[a]		μ_{eff}(BM)[f]	4.58
in nitromethane	6	ϑ(K)[g]	− 3.0
in acetone	8	ligand field (10^3 cm^{-1})	
Molecular weight[b]	456 (449)	diffuse reflectance	
IR (cm^{-1})		$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	20.62 sh, 18.69
Ligand bands[c]		$^4T_{1g} \rightarrow {}^4T_{2g}$	8.73, 8.10
ν(N=N)	1 219 s	calc. $^4T_{1g} \rightarrow {}^4A_{2g}$	17.93
ν(N—N)	1 136 m	other bands	15.27 sh
Nitrate bands[d,e]		10 Dq (cm^{-1})	9 495
$\nu_1(A_1)$	1 429 s	B (cm^{-1})	760
$\nu_4(B_2)$ + [(C—N)]	1 277 sb	β	0.78
$\nu_2(A_1)$	1 017 m	solution (nitromethane)[h]	
$\nu_6(B_1)$	810 m	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	18.97 (295)
$\nu_5(B_2)$	697 w	$^4T_{1g} \rightarrow {}^4T_{2g}$	8.82 (47), 7.99 (39)
ν(Co—ONO$_2$)	300 m, 274 s	10 Dq (cm^{-1})	9 565
		B (cm^{-1})	784
		β	0.81

[a] Values of molar conductivity for a 10^{-3} *M* solution at 25°C

[b] Ebullioscopically in acetone; the required value for the monomer is in parentheses

[c] The IR spectrum of *MeBTA* (not included in the table) exhibits ν(N=N) at 1 196 s and ν(N—N) at 1 108 m cm^{-1}

[d] The $\nu_3(A_1)$ mode of the bidentate C_{2v} nitrato groups was not assigned because the region at ca. 750 cm^{-1} is obscured by strong *MeBTA* bands

[e] The IR spectra of this complex in nujol or hexachlorobutadiene and of its blue powdered KBr pellet differ; the spectrum obtained in KBr is indicative of the presence of ionic D_{3h} nitrates (this is confirmed by the appearance of a new strong band at 1 385 cm^{-1})

[f] Measured at room temperature

[g] The value of Weiss constant was determined from the plot of the reciprocal molar susceptibility corrected for diamagnetism, *vs.* temperature (85–295 K)

[h] Values of molar extinction coefficient ε in l cm^{-1} mol^{-1} are in parentheses

postulating that the six-coordinate complex can be regarded as having a rather distorted quasi-tetrahedral structure with bonds directed toward the centres of the bidentate nitrato groups instead of toward the oxygen atoms. The crystal structure of the trimethylphosphine oxide complex has been determined [18]. It has a distorted *cis* octahedral [Co((CH$_3$)$_3$PO)$_2$(NO$_3$)$_2$] structure, with the nitrate groups chelating, but little distorted from their inherent D_{3h} symmetry; the molecule has no crystallographic symmetry elements, and the only approximate symmetry element is a quasi-twofold axis.

However, the assumption of a quasi-tetrahedral coordination is perhaps unnecessary [16]. These molecules have a distorted six-coordinate structure of C_2 symmetry. The degeneracy of the ground state of the Co(II) ion is lifted ($^4T_{1g}(O_h) \rightarrow {}^4A$, 2 ^4B in C_2). The new orbital singlet ground state gives rise to a magnetic moment much closer to the spin-only value than that observed in a octahedral complex and

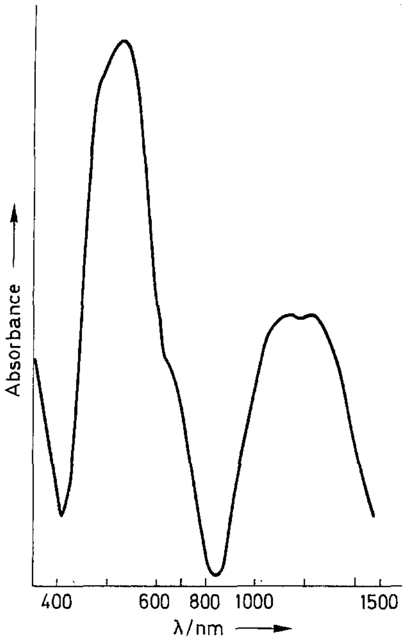


Fig. 1. The electronic diffuse reflectance spectrum of $Co(\mathit{MeBTA})_2(NO_3)_2$

explains the fact that the magnetic moment of $Co(\mathit{MeBTA})_2(NO_3)_2$ is practically temperature independent (very small ϑ value). It should be noted that the method of distinguishing octahedral from tetrahedral complexes by magnetic measurements [13] is really only a way of distinguishing an orbital triplet ground state from an orbital singlet ground state. The experimental magnetochemical data for $Co(\mathit{MeBTA})_2(NO_3)_2$ imply that the complex has an orbital singlet ground state rather than being necessarily tetrahedral. The absence of a center of symmetry could produce a fairly high intensity d-d spectrum since both p and d orbitals span common representations in C_2; this was observed in the present complex. The splitting of the near-IR d-d band in high-spin octahedral Co(II) systems can be regarded as a criterion for distorted *cis* structures.

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