δ_A 4.35 and δ_B 4.08 ppm and $J_{AB} = 13$ Hz. This is consistent with the expected nonequivalence of the tartrate protons. For the neutral species $[Co(en)_2(C_4H_3O_6)]$ the same type of pattern is also observed but is shifted slightly upfield by 0.07 ppm. For both complexes it is envisaged that coordination occurs through a carboxylate group and a deprotonated hydroxyl group. Hence such similarity of the nmr spectra would be anticipated. Moreover, the species $[Co(NH_3)_4(C_4H_4O_6)]Cl$ where such coordination has been shown previously[7] shows a similar AB pattern also with δ_A 4.35 and δ_B 4.14 ppm. This pattern was maintained in acidic or neutral solution with only a slight shift as above and hence further support is given for the nature of the ethylenediamine analogs.

Thus in this study a series of monomeric species have been isolated from mixtures of $[Co(en)_2CO_3]^+$ and tartaric acid. For the D(−) acid the Λ configuration was found while for the L(+) acid the Δ configuration was obtained. These configurations are in agreement with those obtained for the dimeric species[5] obtained earlier from mixtures of those reactants. Hence the exact nature of the product obtained is strongly dependent on the method of preparation but a similar asymmetric bias is imposed for each type of complex.

Acknowledgments. The authors are grateful to the National Research Council of Canada for financial support of this work.

Registry No. Λ-$[Co(en)_2(D(-)\text{-}C_4H_4O_6)]Cl$, 52032-32-3; Λ-$[Co(en)_2(D(-)\text{-}C_4H_3O_6)]$, 52022-19-2; $[Co(en)_2(D(-)\text{-}C_4H_4O_6)]ClO_4$, 52022-20-5; $[Co(NH_3)_4(D(-)\text{-}C_4H_4O_6)]NO_3$, 52019-97-3; $[Co(en)_2CO_3]Cl$, 15842-50-9; $[Co(en)_2CO_3]ClO_4$, 15155-12-1.

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Spin Delocalization in Square-Planar Spin-Triplet Benzene- and Toluenedithiolatocobaltate(III)

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The nature of the ground state and electron delocalization in tetrabutylammonium bis(benzenedithiolato)cobaltate(III) and the corresponding toluene compound has been investigated by far-infrared- and nmr spectroscopy and by measurement of paramagnetic susceptibility. The results are shown to be consistent with a spin-triplet ground state, as predicted by a molecular orbital calculation on the benzenedithiolate. The degeneracy of the ground state is lifted by a zero-field splitting of about 35 cm^{-1}. Of the singly occupied orbitals d_{z^2} and d_{yz}, the latter is considerably delocalized over the ligands.

Introduction

Tetrabutylammonium bis(1,2-benzenedithiolato)cobaltate(III), $Bu_4NCo(bdt)_2$, and tetrabutylammonium bis(3,4-toluenedithiolato)cobaltate(III), $Bu_4NCo(tdt)_2$, are two of the few d^6 transition metal complexes having a triplet ground state.[1-8] Although five- and six-coordinate complexes are known,[1,2] most compounds of this type have a planar four-coordination. Examples are iron(II) phthalocyanine,[3] bis(biuretato)cobaltate(III),[4] bis(aminobenzenethiolato)cobaltate(III),[5] bis(maleonitriledithiolato)cobaltate(III),[6,7] and the bis(benzenedithiolato)cobaltates.[7,8]

Assignments of the ground-state configuration of the MS_4 chromophores in general are few,[9] uncertain,[10,11] and conflicting[10,12-14] although the molecular structures are known. Recently it was even suggested[14] that the ground state of the $Co(tdt)_2^-$ species is actually a spin singlet, the well-established paramagnetism of this compound being caused by a low-lying excited triplet state. Nmr and far-infrared data are conspicuously lacking.

Therefore we have investigated these systems in order to obtain detailed information about the electronic ground state. We have selected magnetic susceptibility and far-infrared techniques to obtain zero-field splittings and *g* values. Proton nmr shifts were recorded at several temperatures for information about the spin density on the ligands and for correlation with a molecular orbital calculation.

Experimental Section

Benzene-1,2-dithiol was prepared as described in the literature.[15] Toluene-3,4-dithiol (Merck) was used without further purification. $Bu_4NCo(bdt)_2$ and the toluene analog were prepared according to the method of Baker-Hawkes[8] and recrystallized three times from CH_2Cl_2 and acetone. The compounds were checked for purity by elemental analyses carried out under supervision of W. J. Buys at the Microanalytical Department of the Institute for Organic Chemistry, TNO Utrecht, The Netherlands.

Nmr spectra were recorded on a Varian XL-100 spectrometer, fitted

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with a variable-temperature cryostat. Powder susceptibility measurements in the 2–100 K range were obtained on a Foner vibrating-sample magnetometer, supplied with a superconducting magnet at a field of 10.7 kG. Measurements were carried out by Dr. H. T. Witteveen[16] at Leiden University. Susceptibilities above 100 K were determined by the Faraday method at a field of 10 kG (using $Ni(en)_3S_2O_3$ as a calibrant). Room-temperature infrared spectra (4000–400 cm^{-1}) of pressed KBr-disk samples were recorded on a Perkin-Elmer 521 spectrometer. Low-frequency spectra (700–200 cm^{-1}) were measured in pressed polythene disks (Merck Uvasol) with a sample concentration of 13% by weight on a Hitachi EPI-L spectrometer. In the 400–20-cm^{-1} range, spectra from the same polythene disks were recorded on a Grubb-Parsons interferometer, both at room temperature and after cooling to approximately 100 K, by Mr. G. van de Langkruis at Leiden University. In order to look for an intratriplet transition, the 150–20-cm^{-1} range was scanned both at room temperature and at a temperature of approximately 15 K on a Polytec FIR 30 interferometer, equipped with a Cryodyne cooler. These measurements were carried out by Dr. Schmidt of Polytec GmbH, Reichenbach, West Germany.

Results

In Figure 1, the choice of the molecular axes in the anion of tetrabutylammonium bis(benzenedithiolato)cobaltate(III), abbreviated as $Bu_4NCo(bdt)_2$, as well as the labeling of the protons, is given. In the corresponding toluene derivative, $Bu_4NCo(tdt)_2$, the methyl groups are assumed to be substituted in positions 4 of the aromatic rings.[17] In the following the results from susceptibility measurements and proton nmr and far-infrared spectra will be presented.

Magnetic Susceptibility. In Figures 2 and 3, the molar susceptibilities χ_M of $Bu_4NCo(bdt)_2$ and $Bu_4NCo(tdt)_2$ and their reciprocals $1/\chi_M$ are presented *vs.* *T*. Susceptibilities were not corrected for diamagnetism or temperature-independent paramagnetism, as these virtually cancel within the error of measurement.

A Weiss constant of approximately zero was found. The drawn curve is a least-squares fit to the experimental values of the expression of the susceptibility of a spin-triplet state in an axially distorted environment as given in eq 1,[18] where

$$\chi_M = \frac{2N\beta^2}{3}\left(\frac{g_\parallel^2 \exp(-D/kT)}{kT[1 + 2\exp(-D/kT)]} + \frac{2g_\perp^2[1 - \exp(-D/kT)]}{D[1 + 2\exp(-D/kT)]}\right) \quad (1)$$

temperature-independent *D* and *g* values are assumed. In the limits of very low and very high temperatures, eq 1 becomes

$$kT \ll D\text{:}\quad \chi_M = \frac{4N\beta^2 g_\perp^2}{3D} \quad (2a)$$

$$kT \gg D\text{:}\quad \chi_M = \frac{2N\beta^2 g_\parallel^2}{3kT} \quad (2b)$$

The resulting parameters for $Bu_4NCo(bdt)_2$ are $D = 37.4$ cm^{-1}, $g_\perp = 2.31$, and $g_\parallel = 2.19$ and for $Bu_4NCo(tdt)_2$ are $D = 39.4$ cm^{-1}, $g_\perp = 2.27$, and $g_\parallel = 2.09$.

A few remarks concerning these fits should be made. The spin-Hamiltonian parameters obtained should not be taken too seriously. Equally convincing fits could be obtained with sets of parameters as widely differing as $D = 42.3$ cm^{-1}, $g_\perp = 2.35$, $g_\parallel = 1.78$ and $D = 34.2$ cm^{-1}, $g_\perp = 2.11$, $g_\parallel = 2.49$ in the $Bu_4NCo(tdt)_2$ case, although these fits are somewhat less satisfactory from the least-squares point of view (variance 25% higher). Thus the powder susceptibility measurements do not allow an unambiguous determination of the *g* anisotropy, as has been pointed out by others.[3] We emphasize however that a large zero-field splitting of the order of 40 cm^{-1} must be present. From 2 to 8 K (eight points measured) the susceptibility of both $Bu_4NCo(bdt)_2$ and $Bu_4NCo(tdt)_2$ remains constant as it should for an axial triplet with a positive *D* of this size. In addition magnetization measurements at 2 K show no apparent saturation up to 55 kG. Although fitting the calculated susceptibility of a triplet with a rhombic spin Hamiltonian to the experimental values is possible in principle and has been tried, it does not result in a unique and reliable set of parameters.

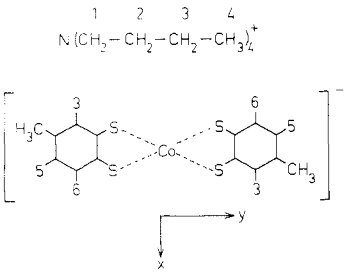

Figure 1. Proton labeling in $Bu_4NCo(tdt)_2$.

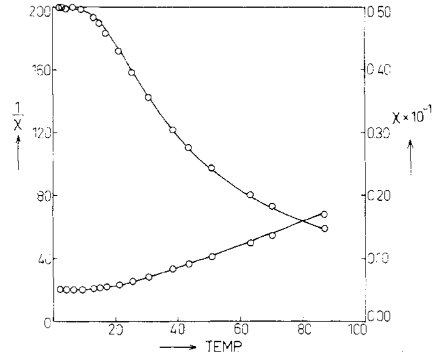

Figure 2. Molar susceptibility χ_M and $1/\chi_M$ *vs.* *T* for $Bu_4NCo(bdt)_2$. Drawn line represents theoretical values, calculated with eq 1 for $D = 37.4$ cm^{-1}, $g_\perp = 2.31$, and $g_\parallel = 2.19$.

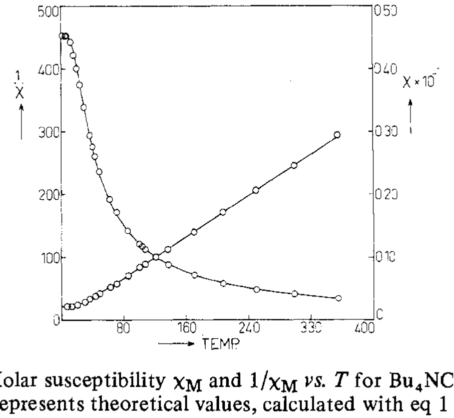

Figure 3. Molar susceptibility χ_M and $1/\chi_M$ *vs.* *T* for $Bu_4NCo(tdt)_2$. Drawn line represents theoretical values, calculated with eq 1 for $D = 39.4$ cm^{-1}, $g_\perp = 2.27$, and $g_\parallel = 2.09$.

The high-temperature magnetic moment found for both compounds is $\mu = 3.12 \pm 0.03$ BM, in agreement with literature reports.[7]

Infrared Spectra. Infrared spectra in the high-frequency region agreed with literature data.[7] The observed bands in the low-frequency region are listed in Table I together with some tentative assignments.

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(16) H. T. Witteveen, Thesis, Leiden, 1973.

(17) In this work, no indications of the existence of a mixture of two species, *viz.*, the cis and the trans isomers of $Co(tdt)_2^-$, have been found even after fractional crystallization of $Bu_4NCo(tdt)_2$.

(18) R. L. Carlin, *J. Chem. Educ.*, **43**, 521 (1966).

Table I. Far-Infrared Absorptions of Cobalt Dithiolates

$Bu_4NCo(bdt)_2$	$Bu_4NCo(tdt)_2$	Tentative assignments[a]
32 w		
34 w[b]	34 w	$M_S = \pm1 \leftarrow M_S = 0$ transition
	44 w	
69 w	71 w	
102 w	103 w	
	135, 144	
162 s	162 s	CoS_4 wag
257 w	242	
287 s	281	CoS_4 bend
298 s		
340 w		
	367 s	CoS_4 str
390 vs	380 s	
	385 vs	
432	419 s	Aromatic ring out-of-plane def
442	438 s	
477	446 vs	
485 w	480	
515 w	498 w	In-plane def
	548 s	Aromatic methyl def
	634 w	
667 s	684 vs	

[a] NBu_4^+ has no strong bands in this region. [b] Intensity increases upon cooling.

Low-frequency electronic transitions are distinguished from phonon bands by their temperature dependence, Zeeman effect, or polarization.[19] On cooling to 15 K the intensity of the 34-cm^{-1} line in the $Bu_4NCo(bdt)_2$ spectrum is remarkably enhanced relative to the other bands (Figure 4). This strongly suggests an intratriplet transition, *i.e.*, between the $M_S = 0$ and the $M_S = \pm1$ components of the triplet ground state, the degeneracy of which is lifted by spin-orbit coupling combined with low-symmetry ligand fields and possibly by spin-spin dipolar interaction in the anion. The zero-field splitting parameter thus directly obtained from the far-infrared spectrum is in good agreement with the D value obtained from susceptibility measurements (*vide supra*). In the $Bu_4NCo(tdt)_2$ spectrum, although much less pronounced than in the spectrum of the benzene compound, there are some indications of a weak, 10 cm^{-1} wide band, centered around 35 cm^{-1}, growing in intensity as the temperature is lowered, which absorption might also be assigned to a transition between the split triplet components. In this case, the larger width of the band might be the result of a larger "rhombicity" in the zero-field splitting (larger E) than in $Bu_4NCo(bdt)_2$.

Proton Magnetic Resonance Spectra. Figure 5 shows a typical nmr spectrum. Line widths as low as 2 Hz have been found. The temperature-dependent chemical shifts of $Bu_4NCo(bdt)_2$ and $Bu_4NCo(tdt)_2$ in several solvents and at different temperatures were measured against internal TMS and are shown in Figures 6-9 relative to the corresponding shifts of the protons of the Cu(III) derivative (which is diamagnetic); assignments are discussed below. The poor solubility of $Bu_4NCo(bdt)_2$ in all common solvents precludes extension of the measurements to low temperatures. With the exception of solutions in $CDCl_3$ and CD_2Cl_2, the Knight shift of the Bu_4N^+ ion protons was very low: in DMSO and acetone the shifts were less than 2 ppm upfield from TMS. In Figures 6-9, shifts are plotted against $1/T$ and straight lines are obtained with nonzero intercepts at $1/T = 0$. Considerable cation proton shifts were measured in $CDCl_3$. From Figures 7-9 it is evident that these shifts as well as those of the $Co(tdt)_2^-$ ion are concentration dependent. In addition, the nmr lines of $Co(tdt)_2^-$ in $CDCl_3$ are split below −40°.

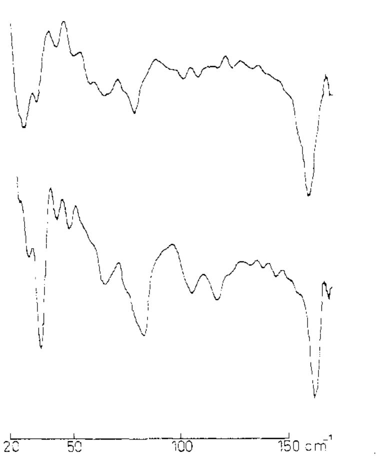

Figure 4. Far-infrared absorption spectrum of $Bu_4NCo(bdt)_2$ in polyethylene at room temperature (upper spectrum) and after being cooled to approximately 15 K (lower spectrum).

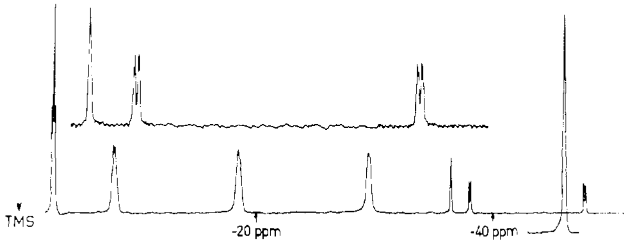

Figure 5. Nmr spectrum of $Bu_4NCo(tdt)_2$ in $CDCl_3$ at 60°. For assignment see text. The upper spectrum is the right-hand part on a larger scale. The strong peak at the right is situated at +38 ppm.

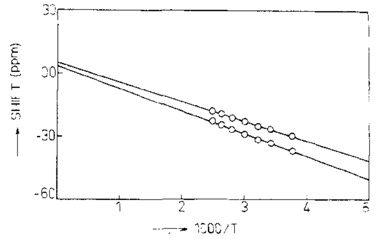

Figure 6. Nmr shifts of $Co(bdt)_2^-$ protons *vs.* $1/T$.

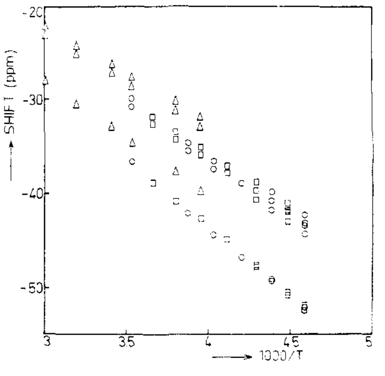

Figure 7. Anion ring proton shifts of $Bu_4NCo(tdt)_2$: ○, concentration 4.5% in $CDCl_3$; □, concentration 3.2% in $CDCl_3$; Δ, concentration 2.8% in acetone-d_6.

Discussion

Magnetic Susceptibility. From the susceptibility measurements it is evident that the ground state of both $Bu_4NCo(bdt)_2$ and $Bu_4NCo(tdt)_2$ is a spin triplet, the degeneracy of

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(19) D. Bloor and G. M. Copland, *Rept. Progr. Phys.*, **35**, 1173 (1972).

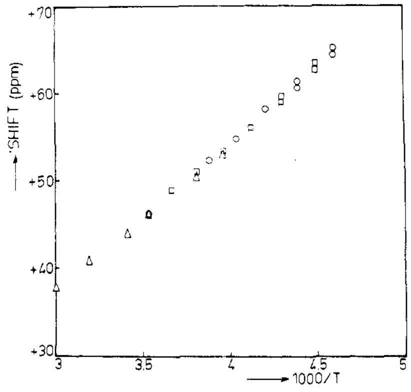

Figure 8. Anion methyl proton shifts of $Bu_4NCo(tdt)$. Concentrations are as in Figure 7.

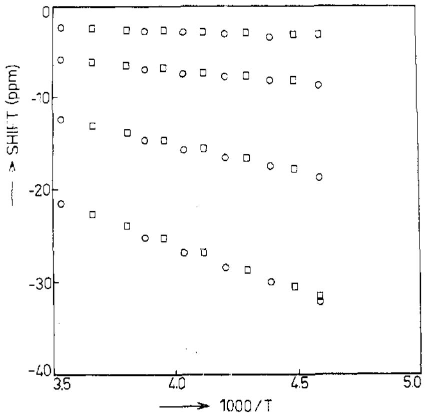

Figure 9. Cation proton shifts of $Bu_4NCo(tdt)$ in $CDCl_3$. Concentrations are as in Figure 7.

which is lifted by a zero-field splitting of approximately 40 cm^{-1}. No indications for the existence of an excited multiplet within 300 cm^{-1} of the ground state were found. This result contradicts measurements on $Bu_4NCo(tdt)_2$ by Ollis, *et al.*,[14] who needed to postulate a singlet ground state 8.5 cm^{-1} below an excited triplet state to explain their susceptibility values which were claimed to show a pronounced maximum near 8 K. We could detect no such maximum at repeated trials with different samples.

The Weiss constant of 14 K as found by Balch, *et al.*,[20] from high-temperature measurements is not observed either. If any antiferromagnetic cooperative effect exists at all, it would be less than 3 K. The average g value is fairly high as is well known for such compounds.[7]

This magnetic behavior is similar to that found in other known planar d^6 triplets. The bis(propylbiuretato)cobaltate(III) is reported[4] to have a zero-field splitting of 40 cm^{-1} and iron(II) phthalocyanine[3] has $D = 64$ cm^{-1} and $g_\parallel = g_\perp = 2.74$. On the contrary, the six-coordinate ferrous diimines[2] have D values as small as 2-3 cm^{-1}, but here a different ground state is suggested.

Far-Infrared Spectrum. The temperature-dependent absorption in the far-infrared spectrum of $Bu_4NCo(bdt)_2$ supports our interpretation of the susceptibility data, although the resulting D value of 34 cm^{-1} (and $E < 5$ cm^{-1}) is smaller than the value deduced from the susceptibility fit of this compound. However, the discrepancy falls within the experimental error. If we take D as 34 cm^{-1}, we can calculate the g anisotropy of $Bu_4NCo(bdt)_2$ from the constant susceptibility below 8 K, which amounts to 0.05 cgsu/mole. Now eq 2a yields the perpendicular g value: $g_\perp = 2.21$. From eq 2b and the high-temperature magnetic moment of 3.13 BM, $g_\parallel$ can be calculated to be 2.24. Any uncertainty in diamagnetism and second-order Zeeman contribution is of course reflected in the deduced g values, but these effects roughly cancel each other as was deduced from a χ against $1/T$ plot.

Proton Magnetic Resonance Spectra. As is well known, proton magnetic resonance spectra of paramagnetic complexes in solution can be obtained if the electron spin relaxation time is sufficiently short.[21,22] Large temperature-dependent shifts are then obtained, proportional to the time-averaged value of the electron spin. The hyperfine fields at the proton sites are determined by two quantities: (1) the hyperfine coupling constant, a measure of the spin density at the nucleus, and (2) the anisotropy in the susceptibility if present; this implies that the magnetic dipole-dipole interaction between electron and nuclear spin is not averaged to zero by tumbling in the liquid. The two effects are the Fermi-contact shift and pseudocontact shift, respectively.

The measured proton shifts allow determination of the hyperfine coupling constant[23,24] from eq 3, which obtains

$$\frac{\Delta\nu_k}{\nu_0} = \frac{A_k}{3(\gamma_N/2\pi)\beta N}\left(\frac{\chi_\parallel}{g_\parallel} + 2\frac{\chi_\perp}{g_\perp}\right) \qquad (3)$$

for the axial case, in which $\Delta\nu_k$ is the corrected frequency shift of proton k, ν_0 is the operating frequency of the spectrometer, A_k is the hyperfine coupling constant of proton k in Hz, γ_N is the nuclear magnetogyric ratio, β is the Bohr magneton, and χ is the molar susceptibility in cgsu/mol. The observed chemical shifts must be corrected for the pseudocontact interaction which is determined by eq 4, in

$$\frac{\Delta\nu_k}{\nu_0} = \frac{1}{3N}\left(\chi_\parallel - \chi_\perp\right)\frac{3\cos^2\theta_k - 1}{|r_k|^3} \qquad (4)$$

which θ_k is the angle between the magnetic z axis and the vector r_k, which connects the origin (in which the unpaired electrons are assumed to be concentrated) with proton k.

Application of the pseudocontact correction requires knowledge of not only the anisotropy of the susceptibility but also the relative orientation of magnetic and molecular axes. In the absence of single-crystal magnetic data, we have to proceed with the powder susceptibility results. In the following, axial magnetic symmetry will be assumed.

(a) $Bu_4NCo(bdt)_2$. At the temperatures of the nmr measurements, the anisotropy of the susceptibility is mainly the result of g anisotropy, the zero-field splitting contributing very little.

The nearly isotropic g values induce a rather small pseudocontact shift of the aromatic protons, amounting to 2-6% of the experimental shifts, depending on the magnetic axis orientation. If the experimental shifts are corrected for this, the hyperfine coupling constants in Table II are the result. The lack of information concerning the orientation of the magnetic axis is unimportant in this case, due to the small pseudocontact shifts.

Assignment of the spectrum follows from the change on methyl substitution in the 4 position (Figure 5). The two

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(20) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).

(21) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

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Table II. Hyperfine Coupling Constants (MHz) in $Co(bdt)_2^-$ for Ring Protons 3 and 4[a]

Temp, °C	X		Y		Z		Solvent
	3	4	3	4	3	4	
130	−0.316	−0.401	−0.302	−0.392	−0.320	−0.402	DMSO-d_6
108	−0.321	−0.408	−0.307	−0.397	−0.328	−0.409	DMSO-d_6
85	−0.328	−0.416	−0.314	−0.404	−0.336	−0.416	DMSO-d_6
60	−0.335	−0.420	−0.316	−0.406	−0.342	−0.420	DMSO-d_6
38	−0.341	−0.428	−0.322	−0.413	−0.351	−0.428	DMSO-d_6
20	−0.341	−0.422	−0.321	−0.405	−0.352	−0.422	Acetone-d_6
−7	−0.347	−0.428	−0.324	−0.409	−0.359	−0.429	Acetone-d_6

[a] Columns marked X, Y, and Z contain A_k values after correction for the pseudocontact shift with the magnetic axis parallel to the molecular *x*, *y*, and *z* axis respectively; $D = 34$ cm^{-1}, $g_\perp = 2.21$, and $g_\parallel = 2.24$.

high-field lines show an ortho coupling of 7 Hz originating from ring protons 5 and 6. An unresolved meta coupling of 1 Hz on the highest field line confirms the assignment of the lines upfield from TMS: cation, 4, 3, 2, 1; anion, 3, 6, 5.[25]

(b) $Bu_4NCo(tdt)_2$. The nmr spectrum of the toluene compound in $CDCl_3$ shows large upfield cation shifts as well as the shifted anion lines, which indicates a high degree of ion pairing in this solvent. In acetone and DMSO, the cation shifts were about as small as in the corresponding $Bu_4NCo(bdt)_2$ solutions. The cation shifts which are mainly, if not entirely, due to dipolar coupling, can be used to derive the pseudocontact corrections for the anion proton shifts. The shifts of the corresponding protons in the four butyl chains are equivalent: four lines only are observed at all temperatures,[26] which means that the cation, while associated, is rapidly tumbling about its nitrogen center. Now the geometrical factor $(3 \cos^2 \theta - 1)/r^3$ has to be averaged over the tumbling motion. La Mar[27] has carried out the necessary averaging, including rotation about the C–C bonds in the butyl chains, for the two proton species nearest to the nitrogen atom, H_1 and H_2, respectively. Application of his results to our problem yields a mean distance of 3.7 Å between the Co and N centers of the anion and cation. From this distance an average geometrical factor $\langle(3 \cos^2 \theta - 1)/r^3\rangle$ of 0.035 and 0.024 Å^{-3} for cation protons H_1 and H_2, respectively, can be calculated, assuming that the cation associates along the molecular *z* axis of the anion. These geometrical factors, together with the observed H_1 and H_2 cation shifts, yield the anisotropies in the susceptibility listed in Table III. For comparison the anisotropies calculated from the susceptibility fit are also listed.

The similarity of these anisotropy values obtained from an entirely independent method means as excellent a confirmation of the parameters from the susceptibility measurements as can reasonably be expected of these methods. The magnetic axis can therefore be taken as perpendicular to the molecular plane. Now the pseudocontact corrections to the experimental ligand proton shifts can be calculated from their known geometrical factors.[28] The resulting hyperfine coupling constants are given in Tables IV and V.

Table III. Susceptibility Anisotropy of the $Co(tdt)_2^-$ Ion in $CDCl_3$[a]

Temp, °C	Concn[b]	$10^3(\chi_z - \bar{\chi}_\perp)$ from cation shifts		$10^3(\chi_\parallel - \chi_\perp)$ from susceptibility fit
		H_1	H_2	
+10	a	−1.13	−0.97	−1.09
0	b	−1.18	−1.02	−1.15
−10	b	−1.25	−1.08	−1.21
−15	a	−1.31	−1.14	−1.24
−20	b	−1.32	−1.14	−1.27
−25	a	−1.40	−1.22	−1.30
−30	b	−1.40	−1.21	−1.35
−35	a	−1.49	−1.29	−1.39
−40	b	−1.50	−1.29	−1.43
−45	a	−1.57	−1.36	−1.47
−50	b	−1.60	−1.38	−1.52
−55	a	−1.68	−1.46	−1.57
−55	b	−1.66	−1.43	−1.57

[a] Values in column 5 were calculated with $D = 39.4$ cm^{-1}, $g_\parallel = 2.09$, and $g_\perp = 2.27$. [b] Concentrations: a, 4.5%; b, 3.2%.

Table IV. Hyperfine Coupling Constants (MHz) of the $Co(tdt)_2^-$ Ion Protons Calculated from Anion Shifts in $CDCl_3$

Temp, °C	Concn[a]	Protons			
		3	6	5	Methyl
+10	a	−0.427	−0.437	−0.473	+0.544
0	b	−0.437	−0.447	−0.484	+0.555
−10	b	−0.443	−0.453	−0.490	+0.558
−15	a	−0.449	−0.458	−0.496	+0.562
−20	b	−0.447	−0.456	−0.494	+0.562
−25	a	−0.456	−0.465	−0.503	+0.565
−30	b	−0.454	−0.461	−0.499	+0.566
−50	b	−0.467	−0.466	−0.517	+0.585
−55	a	−0.472	−0.480	−0.521	+0.588
−55	b	−0.471	−0.478	−0.520	+0.588

[a] See footnote *b* of Table III.

Table V. Hyperfine Coupling Constants (MHz) of the $Co(tdt)_2^-$ Ion Protons Calculated from Anion Shifts in Acetone-d_6

Temp, °C	Protons			
	3	6	5	Methyl
+60	−0.376	−0.389	−0.428	+0.522
+40	−0.386	−0.399	−0.439	+0.530
+20	−0.392	−0.404	−0.442	+0.534
+10	−0.399	−0.411	−0.449	+0.542
−10	−0.406	−0.418	−0.456	+0.550
−20	−0.413	−0.424	−0.462	+0.557

Besides being slightly solvent and concentration dependent, the A_k values of both $Co(bdt)_2^-$ and $Co(tdt)_2^-$ protons are temperature dependent, not only in $CDCl_3$, in which the ions are associated, but also in solvents where little ion pairing occurs. Temperature-dependent hyperfine coupling constants have often been observed[29-32] in esr spectra of organic radicals or transition metal complexes. Hence the general occurrence of nonzero shift-axis intercepts at $1/T = 0$, even after correction for a non-Curie-type behavior according to

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(25) If however introduction of the methyl group in the 4 position drastically changes the ring π-spin density, which is unlikely, the given assignment of the $Co(bdt)_2^-$ proton lines in Table II might have to be reversed.

(26) Assignments as given by G. N. La Mar, *J. Chem. Phys.*, 41, 2992 (1964).

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eq 3 and 4, is not surprising and any successful fit[33] of shifts to the restricted Kurland–MacGarvey equations (*i.e.*, eq 3 with temperature-independent A_k and eq 4) may be considered as accidental.

Molecular Orbital Calculations. A semiquantitative MO calculation has been performed on the Co(bdt)$_2^-$ ion according to a method as proposed by Hillier.[34] Details are available upon request. The resulting ground-state configuration is $(a_g)^1(b_{3g})^1$. The a_g orbital is mainly metal-based d_{z^2} and has some $d_{x^2-y^2}$ character. Its spin density at the ligand protons is calculated to be responsible for less than 1% of the observed shifts. Almost half of the b_{3g} orbital is metal based (d_{yz}). Approximate A_k values are calculated using McConnell's relation[21] $A = Q\rho_k/2S$ in which $Q = -63$ MHz and ρ_k is the π-spin density at the carbon atom next to the proton, *i.e.*, the carbon 2 p_z atomic orbital coefficients squared. A more sophisticated approach was not considered useful because of the approximate nature of the MO calculation. The results $A_3 = A_6 = -0.507$ MHz and $A_4 = A_5 = -0.306$ MHz are of the same order of magnitude as those found from the nmr shifts given in Tables IV and VI; however, experimentally $A_3 < A_4$ whereas the reverse is found in the calculation. The composition of the singly occupied a_g MO could in principle be estimated from D and g values. Estimates of g values, considering one-center angular momentum matrix elements of the metal and sulfur atoms only, could account for no more than half of the measured deviation from the free-electron g values.

A more advanced calculation including configuration interaction is in progress. In spite of the discrepancies in the admittedly rough MO calculation and derivation of the spin-Hamiltonian parameters and notwithstanding different proposals by others on the same[7] or similar[3,4] compounds, we feel confident that our calculated ground state is qualitatively correct. Most planar d^7 systems have one unpaired electron either in a d_{yz} orbital,[13,35] like Ni(mnt)$_2^-$ or Co(mnt)$_2^{2-}$, or in a d_{z^2} orbital, like Co(sacsac)$_2$ or cobalt phthalocyanine.[36,37] Moreover, the large in-plane g anisotropies in Co(mnt)$_2^{2-}$ and Co(sacsac)$_2$ are explained in terms of a relatively small separation between the d_{z^2} and the d_{yz} orbitals, which might indicate that the d_{z^2} orbital in our complexes is unlikely to be very far removed from the d_{yz} orbital.

Final Remarks

From the arguments discussed above, we conclude that the ground state of bis(benzenedithiolato)cobaltate(III) and the toluene derivative is a spin triplet with a large zero-field splitting. The semiquantitative MO calculation suggests that the preponderant configuration of the ground state $^3B_{3g}$ is $(a_g)^1(b_{3g})^1$ in which a_g is predominantly d_{z^2} and b_{3g} is half d_{yz}. The spin densities in the aromatic ligand rings are then caused by direct π delocalization of the b_{3g} unpaired electron.

The nmr results indicate that substitution of the methyl group in the benzenedithiolate has two effects: it increases the spin density in the singly occupied π^* orbital of the aromatic ring and it increases the magnetic anisotropy, mainly by the g values. As stated above, we have not yet been able to determine an accurate D value of Bu$_4$NCo(tdt)$_2$.

Assumptions inherent in the above treatment of the Co(tdt)$_2^-$ shifts are worth summarizing.

1. Coupling constants in Table V were calculated assuming that the magnetic axis is perpendicular to the plane of the anion. However $\overline{\chi_\perp}$ in Table III is the rotationally averaged in-plane susceptibility, since the associated cation is not fixed. This means that it still is perfectly possible for the magnetic axis to lie in the plane of the anion. If it lies in the y direction, it would certainly modify the pseudocontact shifts and hence the resulting A_k of the anion. Results from additional far-infrared experiments are expected to settle the issue.

2. The anisotropies mentioned in columns 3 and 4 of Table III were calculated from exchange-averaged H_1 and H_2 cation shifts and must therefore be considered lower limits to the anion anisotropy. We suspect however that the association is fairly complete and extrapolation to 100% ion pairing would constitute no more than a second-order correction to the A_k of the anion.

3. Coupling constants in Table V were obtained from experimental anion shifts measured in acetone-d_6, whereas pseudocontact corrections were taken from cation shifts in associated ion pairs in CDCl$_3$ solution. Changes in magnetic properties of the anion on ion association are assumed to be small because shift changes are.

4. Fermi-contact interaction on the cation protons, induced by ion pairing, has been shown to exist.[38] Again in our case this would be a small correction and can safely be ignored.

5. The associated cation is assumed to be centered on the z axis of the anion in La Mar's averaging procedure while from the Co(tdt)$_2^-$ shifts in CDCl$_3$ below −40° it seems that the associated cation jumps from one negatively charged part of the anion to the other, over the potential barrier of the positively charged Co center. At 0°, the jumping rate is fast compared to the shift differences (40–120 Hz) but at −55° it is slow enough to distinguish two sets of nonequivalent anion protons. How this jumping affects La Mar's average geometrical factors of the cation protons is not clear. As the resulting cation–anion distance is reasonable, we feel that this effect can be considered as a second-order correction.

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Registry No. Bu$_4$NCo(bdt)$_2$, 15186-37-5; Bu$_4$NCo(tdt)$_2$, 52152-15-5.

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