a strongly tetragonally compressed tetrahedron than a square plane. Also the rigid bipyridyl ligand cannot occupy two equatorial positions of a TBP because the chelate $N_{1(3)}$–Cu–$N_{2(4)}$ angle is fixed to about 80°. Thus, a TBP, with two N atoms of different bipyridyl molecules in the axial positions, or a SP, in which one bidentate ligand bridges the apical and one equatorial site, is expected to be the preferred geometry, if ligand effects were dominating. The $[Cu(N_1N_2)(N_3N_4)NH_3]^{2+}$ polyhedra in $[Cu(bpy)_2NH_3](BF_4)_2$ with five Cu–N bonds, for example, constitute in first approximation trigonal bipyramids.[35] They are axially compressed, however, due to the electronic effect of the d^9-configurated Cu^{2+} ion because stronger axial and weaker equatorial bonds will lower the energy of the A_1' ground state in D_{3h} symmetry (Figure 1). A closer look into the equatorial plane of the Cu^{2+} polyhedra reveals that the equatorial Cu–N_2 bond length is significantly larger than the other two (Table I). Also the equatorial angle opposite to this bond direction is much larger than 120°. Clearly these geometrical deviations can be understood as a step along the pathway from a compressed TBP to an elongated SP (Figures 1 and 5). The observation of an intermediate coordination geometry is analogous to what has been found for $[Cu(tren)NCS]^+$, discussed above. A more detailed analysis of the Cu–N spacings and NCuN bond angles leads to a model in which an elongation along Cu–N_4—with less statistical weight—superimposes the one along Cu–N_2. An even more pronounced deviation toward a square pyramid is found for the $[Cu(NN)_2NCS]^+$ cation in $[Cu(bpy)_2NCS]BF_4$[36] (Table I). For $[Cu(NN)OH_2]^{2+}$, two interesting alternative cases are found. One ($S_5O_6^{2-}$ as counterion) parallels the examples before—elongation of the Cu–N_2 bond; the other one ($S_2O_6^{2-}$ as anion) implies an elongation along the Cu–O bond direction.[37] The substitution of the weaker ligand Cl^- into the fifth coordination site leads again to compressed trigonal bipyramids, in which also sometimes one equatorial Cu–N bond is distinctly larger, however. The structural profile of CuN_4Cl in various compounds is discussed in detail by Hathaway and co-workers.[38] It is always open to question whether in cases where only structural data at 298 K are available, dynamic averaging effects are present or not. The EPR spectroscopic investigation of some representative examples down to 4.2 K gives evidence, however, that the observed geometry is static.[7]

Concluding, one may state that the geometry of 5-coordinate Cu^{2+} polyhedra with multidentate ligands is determined equally by steric ligand and by electronic effects (Table I). While the former may stabilize—depending on the specific geometry and rigidity of the ligand—any square-pyramidal, trigonal-bipyramidal, or intermediate geometry (Figure 5), the latter always induce the expected bond length anomalies. These are a *compressed* TBP, an *elongated* SP, or any intermediate conformation.[39]

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Registry No. $[Co(NH_3)_6]CuCl_5$, 16028-79-8; [*N*-(2amet)-pipzH_3]$CuCl_5$, 73245-69-9; [dienH_3]$CuCl_5$, 56508-39-5; [Cu(tren)-NCS]SCN, 18582-12-2.

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Electronic Structure of the Nitroxyl Complex Bis(di-*tert*-butyl nitroxide)cobalt(II) Bromide

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The magnetic and EPR properties of the nitroxyl complex bis(di-*tert*-butyl nitroxide)cobalt(II) bromide have been reexamined. It is concluded that the ground state is a spin doublet, as shown by the magnetic susceptibility and the EPR spectra at liquid-helium temperature. The *g* values, which show large deviations from the free-electron value, are rationalized in terms of a sum of contributions from the radicals and the high-spin cobalt(II) ion.

Nitroxyl radicals are known to act as weak Lewis bases[1,2] and are widely used as spin probes in biological systems[3–6] and as ligands for a variety of transition-metal ions.[3,7–9] The complexes in which the nitroxyl group is directly bound to the metal ion are of particular interest for the mechanism of coupling of the unpaired electrons of the ligand and of the metal, but not many well-characterized examples are available. The extent of coupling has been found to vary from weak to strong, depending on the relative geometry of the magnetic orbitals of the metal and of the free radical.[2,10–12]

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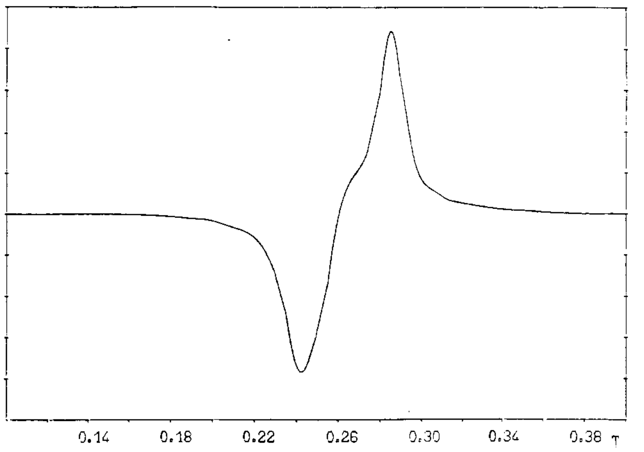

Figure 1. Liquid-helium-temperature EPR powder spectra of $CoBr_2(DTBNO)_2$.

One of the first reported examples of a stable transition metal ion–nitroxyl complex is $CoBr_2(DTBNO)_2$ (DTBNO = di-*tert*-butyl nitroxide), whose magnetic properties and consequently the spin degeneracy of the ground state are still controversial.[13,14]

Beck et al.[13] reported a room-temperature magnetic moment of 2.59 μ_B, which decreases to 2.43 μ_B at 195 K and to 2.32 μ_B at 77 K and concluded for a ground spin doublet. Brown et al.,[14] on the other hand, reported an almost temperature-independent moment of 4.2 μ_B from 4.2 to 300 K and concluded for a ground quartet. Also, the liquid-nitrogen-temperature EPR spectra were interpreted in two different ways, as indicative of a spin doublet or of a spin quartet experiencing a large zero-field splitting, respectively.[13,14] We wish to report here new EPR and magnetic susceptibility data with the aim of characterizing the nature of the ground state of this complex.

Experimental Section

DTBNO was prepared as previously described.[15] Freshly distilled nitroxide and anhydrous $CoBr_2$ in molar ratio 5:1 were allowed to react for 5–6 h at room temperature, under rigorously anhydrous nitrogen atmosphere. Dry benzene was added and the solution filtered to remove unreacted $CoBr_2$. The solution was reduced to small volume until precipitation occurred. The dark green compound gave a satisfactory analysis for $CoBr_2(DTBNO)_2$. (Anal. Calcd for $CoBr_2C_{16}H_{36}N_2O_2$: C, 37.88; H, 7.15; N, 5.52. Found: C, 37.52; H, 7.35; N, 5.40.)

The magnetic susceptibility measurements were performed with a Faraday balance employing a Cahn R-100 microbalance and a Bruker B-N50 magnet. Variable-temperature measurements were performed with a CF 200 Oxford Instruments continuous-flow cryostat. The internal helium pressure was adjusted at 10^{-1} mmHg.

Results and Discussion

$CoBr(DTBNO)_2$ was found to be only relatively stable. In particular room-temperature EPR spectra showed increasing amounts of free DTBNO when the compound was allowed to stand, especially in the presence of humidity.

The liquid-helium-temperature EPR spectrum (Figure 1) shows a dominant species characterized by three g values, $g_1 = 2.28$, $g_2 = 2.50$, and $g_3 = 2.68$, practically identical with those reported at higher temperature.[14,15] Other signals attributable to free DTBNO and to normal high-spin cobalt(II) species are present in varying concentrations in different samples. No other signal that can be attributed to $CoBr_2(DTBNO)_2$ was recorded in the range 4.2–300 K.

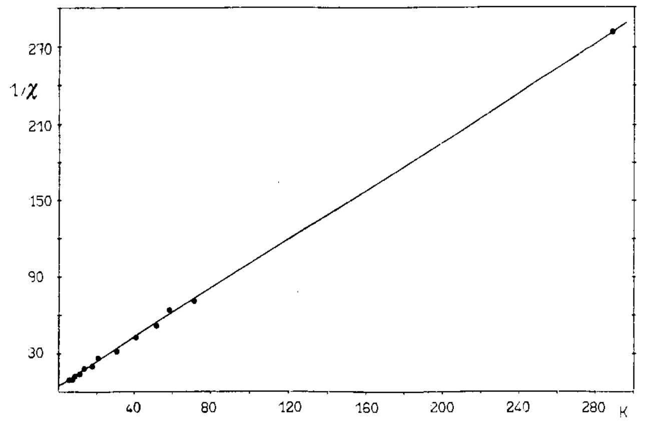

Figure 2. Temperature dependence of the magnetic susceptibility of $CoBr_2(DTBNO)_2$ in the range 4.2–100 K.

Table I. Energies and g Tensors for a Coupled Symmetric System with Three Spins, $S_1 = S_3 = {}^1/_2$ and $S_2 = {}^3/_2$

multiplet[a]	energy	g values[b]
$\lvert {}^5/_2\rangle$	${}^3/_2J + {}^1/_4J'$	${}^2/_5g_{1/2} + {}^3/_5g_{3/2}$
$\lvert {}^3/_2,1\rangle$	$-J + {}^1/_4J'$	${}^4/_{15}g_{1/2} + {}^{11}/_{15}g_{3/2}$
$\lvert {}^3/_2,0\rangle$	$-{}^3/_4J'$	$g_{3/2}$
$\lvert {}^1/_2\rangle$	$-{}^5/_2J + {}^1/_4J'$	$-{}^2/_3g_{1/2} + {}^5/_3g_{3/2}$

[a] The two $S = {}^3/_2$ states are labeled also through the intermediate spin $S' = S_1 + S_3$. [b] $g_{1/2}$ and $g_{3/2}$ refer to individual spins with the indicated S_i values.

The magnetic moment of $CoBr_2(DTBNO)_2$ is dramatically affected by decomposition: in a sample, prepared in a glovebox, it varies from 2.91 to 4.03 μ_B after standing for 12 h in the air and in general we found higher moments for aged samples. One of the best samples we obtained gave a room-temperature moment of 2.86 μ_B in fair agreement with the values reported by Beck et al.,[13] but substantially lower than the value reported by Brown et al.[14] Since clearly decomposed samples have higher magnetic moments, and since it is more reasonable to conceive paramagnetic impurities which increase the moment rather than diamagnetic ones which depress it, we feel that the values reported by Beck et al.[13] are the best approximation of the actual magnetic moment of the $CoBr_2(DTBNO)_2$ species. We also measured the magnetic susceptibility of the sample at 4.2 K and found it to correspond to a magnetic moment of 2.15 μ_B. Since our room-temperature magnetic moment is higher than that reported by Beck,[13] we presume that our sample is less pure; therefore the temperature dependence of the magnetic susceptibility (Figure 2) is certainly affected by an error. Our values are found to follow a Curie–Weiss law, down to 4.2 K $\chi = X/(T + \Theta)$, with $\Theta = 5.1$ K. In any case the low-temperature value, together with the EPR data, can be interpreted only with the assumption of a ground spin doublet state. The suggestion of a ground spin quartet[14] must be discarded, even if the possibility of a large zero-field splitting is taken into account, since in that case at least one g value larger than 4 would be anticipated.[16]

The electronic spectra of $CoBr_2(DTBNO)_2$ were convincingly interpreted[15] to show that the cobalt(II) ion has a formal oxidation state of +2 and that it would be in the usual high-spin state, $S = {}^3/_2$, were it not for the presence of the two free radicals. The fact that the magnetic susceptibility is indeed

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temperature dependent shows that the coupling between the spins is not complete, so that in order to describe the lowest energy levels of CoBr$_2$(DTBNO)$_2$ the exchange spin Hamiltonian[17] can be used

$$H = J(S_1 \cdot S_2 + S_2 \cdot S_3) + J' S_1 \cdot S_3 \qquad (1)$$

where 1 and 3 refer to the two nitroxide spins, $S_1 = S_3 = {}^1/_2$, and 2 to the cobalt center, $S_2 = {}^3/_2$. Coupling the three spins yields one sextet, two quartets, and one doublet state, whose energies are given in Table I.

It is apparent that the spin doublet is the ground state if J is positive and J' negative or, when both J and J' are positive, if $J > {}^2/_5 J'$. Despite the fact that the magnetic susceptibilities are affected by an error, it may be concluded, with use of the high-temperature data of Beck et al.[13] and our liquid-helium data, that J must be antiferromagnetic and must be larger than 200 cm^{-1}, showing that the metal and ligand spins must be fairly substantially coupled in this pseudotetrahedral complex. J' remains largely undetermined.

The experimental g values show large deviations from the free-electron value, which at first glance are surprising. However, they can be easily rationalized by using the relations of Table I, which relate the g values of the individual spins and those of the coupled system. These relations were obtained according to an extension of the procedures normally used for calculating the g values of pairs.[17–19] In fact the two spins S_1 and S_3 may be coupled first to give an intermediate spin S' to which the usual formulas to calculate g can be applied. Then S' is coupled to S_2, again with the g values calculated in the coupled representation S.

The free radical can be reasonably assumed to have an isotropic **g** tensor, $g_{1/2} = 2.00$. With use of the relations of Table I, the g value of the cobalt ion is not known, but for the radical the values of $g_{3/2}$ can be calculated from the experimental data as $g_{1,3/2} = 2.17$, $g_{2,3/2} = 2.30$, and $g_{3,3/2} = 2.41$. These values compare favorably with those previously reported for the pseudotetrahedral complex CoCl$_2$(Ph$_3$PO)$_2$: $g_\parallel = 2{,}31$, $g_\perp = 2.35$. The orthorhombic symmetry of the g values of the CoBr$_2$(DTBNO)$_2$ complex may reflect a more distorted coordination environment for the latter. On the other hand, the high sensitivity of the g values of high-spin cobalt(II) to distortions in the coordination sphere are now well-known.[16]

In conclusion low-temperature magnetic susceptibility and EPR data show that the ground state of CoBr$_2$(DTNBO)$_2$ is a spin doublet originating from the antiferromagnetic coupling between the cobalt and free-radical magnetic orbitals.

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Registry No. CoBr$_2$(DTBNO)$_2$, 34923-18-7.

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Interaction of Dioxygen with Binuclear Nitride-Bridged Iron Porphyrins

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An unusual interaction between O$_2$ and nitride-bridged iron porphyrin dimers in frozen polar glasses has been found. The EPR spectrum previously attributed to a pyridine monoadduct of (μ-nitrido)bis[(5,10,15,20-tetraphenylporphinato)iron] is in fact due to an O$_2$ adduct of the dimeric porphyrin. Optical spectroscopy shows that the O$_2$/porphyrin interaction is weak. Mössbauer spectra demonstrate that the two iron ions are inequivalent in the adduct while EPR data indicate a less anisotropic g tensor and appreciably diminished ^{14}N and ^{57}Fe hyperfine coupling relative to the nonadducted species. O$_2$ titrations, as monitored by EPR, show that the adduct's stoichiometry is one O$_2$ per dimer. All these data are consistent with a weak axial interaction of O$_2$ with one side of the μ-nitrido dimer.

Introduction

The interaction of O$_2$ with metalloporphyrins has been of continued intense study. Several O$_2$ complexes of iron(II) porphyrins, analogous to those of myoglobin and hemoglobin, have been exhaustively examined.[2] Little has been reported, however, on the interaction of higher oxidation state iron porphyrin complexes with O$_2$. We describe here the complexation of O$_2$ to (μ-nitrido)bis[(porphyrinato)iron] dimers in frozen polar glasses.

The nitride-bridged iron porphyrin dimer[3] ((TPP)Fe)$_2$N has been the subject of a number of recent experimental[4–9] and

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[3] Abbreviations: (μ-nitrido)bis[(5,10,15,20-tetraphenylporphinato)iron], ((TPP)Fe)$_2$N; (μ-nitrido)bis[(2,3,7,8,12,13,17,18-octaethylporphinato)iron], ((OEP)Fe)$_2$N; (μ-nitrido)bis{[5,10,15,20-tetrakis-(3,4,5-trimethoxyphenyl)porphinato]iron}, ((TTMPP)Fe)$_2$N; electron paramagnetic resonance, EPR; highest occupied molecular orbital, HOMO.

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