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# Some Divalent 3d Metal Perchlorate Complexes with the 2,2,6,6-Tetramethylpiperidine Nitroxide Free Radical*

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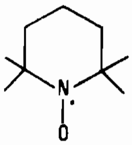
*Interaction of 2,2,6,6-tetramethylpiperidine nitroxide free radical (AMPNO·) with 3d metal perchlorates, in the presence of triethyl orthoformate, leads to the formation of* $M(ClO_4)_2 . TMPNO\cdot$ *(M = Co, Ni) and* $M(ClO_4)_2 . 2TMPNO\cdot$ *(M = Fe, Zn) complexes. Characterization studies suggest that the new complexes are most probably bi- or poly-nuclear, with terminal TMPNO·, a bidentate perchlorato ligand, and a bridging perchlorato group. Magnetic susceptibility and esr data were interpreted in terms of partial spin-spin coupling between the unpaired ligand- and d-electrons, in the paramagnetic metal ion complexes; in the* $Zn^{II}$ *complex partial spin-spin coupling between the unpaired electrons of different ligand molecules occurs.*

## Introduction

The chemistry of stable nitroxide free radicals of secondary amines has been the subject of many studies in recent years.[1,2] An important application of compounds of this type is their utilization as spin labels for probing biomolecular structure.[3] Quite recently, several studies dealing with metal complexes of nitroxide free radicals, involving coordination to the metal ions through either the N-O group[4-12] or other functional groups of the ligand,[9,13] appeared in the literature. Thus, complexes of the following types have been isolated: $Co(DTBNO\cdot)_2X_2$ (DTBNO· = di-*tert*-butyl nitroxide radical; X = Cl, Br, I),[5,12] $[Pd(DTBNO\cdot)X]$ (X = Cl, Br),[6] $Pd(porphyrexide)Cl_2$,[13] $MX_3 \cdot L$ (M = $B^{III}$, $Al^{III}$, $Ga^{III}$; X = F, Cl, Br, I; L = DTBNO·,2,2,6,6-tetramethylpiperidine nitroxide radical (TMPNO·; I), 2,2,6,6-tetramethyl-4-piperidone nitroxide radical),[7,8] $Cu(HFA)_2 \cdot DTBNO \cdot$ (HFA = hexafluoroacetylacetonato ligand),[10] the $Cu^{II}$ salt of 2,2,5,5-tetramethyl-3-carboxypyrroline nitroxide radical,[4] and adducts of cobalamin with various nitroxide radicals.[9] The formation of adducts between $CuSO_4$[4] or 3d metal β-ketoenolates[10,11] and nitroxide free radicals has been studied in solution.



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In a recent communication we reported that interaction of TMPNO· with divalent 3d metal perchlorates (M = Mn through Zn) results in the formation of complexes, and described the decomposition reactions of the labile $Cu^{II}$ complex.[14] The present paper deals with the syntheses and characterization of stable complexes of the types $M(TMPNO\cdot)(ClO_4)_2$ (M = Co, Ni) and $M(TMPNO\cdot)_2(ClO_4)_2$ (M = Fe, Zn).

## Experimental Section

TMPNO· was prepared by the method of Rassat *et al.*,[15] further purifed by vacuum sublimation, and its structure and purity were confirmed by means of its esr, $^1H$ nmr, ir and uv-visible spectra.[15] Crystalline, atmospherically stable, $M(ClO_4)_2 \cdot TMPNO \cdot$ complexes (M = Mn, Fe, Co, Ni, Zn) were synthesized by the following procedure: 0.007 mole of TMPNO· and 0.00175 mole of the hydrated metal perchlorate were separately dissolved in the minimum required amount of triethyl orthoformate, a dehydrating agent.[16]

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The two solutions were then mixed and allowed to stand at room temperature for 1-2 days. Subsequent addition of anhydrous diethyl ether led to the precipitation of the new complexes, which were filtered, washed with triethyl orthoformate and ether, and dried under reduced pressure.

Several attempts to obtain the brown Mn$^{II}$ complex in a sufficiently pure form were unsuccessful; this compound, which is probably of the type $Mn_2(TMPNO\cdot)(ClO_4)_4$ (Found (calcd)%: C 17.92 (16.28), H 3.88 (2.73), N 2.32 (2.13), Mn 17.61 (16.40)), was not studied any further. Fe$^{II}$ and Zn$^{II}$ perchlorates formed 1:2 complexes with TMPNO·, while Co$^{II}$ and Ni$^{II}$ perchlorates yielded 1:1 complexes with this ligand. Analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.) are given in Table I.

**Table I.** Analyses, Colors and Magnetic Moments (294°K) of TMPNO . Metal Complexes

| | | | | | Analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C% | | H% | | N% | | Metal % | |
| | Color | $10^6\chi_g$,cgsu | $10^6\chi_A^{corr}$,cgsu [a] | $\mu_{eff}$,BM [a] | Calc | Found | Calc | Found | Calc | Found | Calc | Found |
| $Fe(ClO_4)_2\cdot 2TMPNO\cdot$ | Brown | 10.27 | 6130 | 3.83 | 38.11 | 37.69 | 6.40 | 6.12 | 4.94 | 4.47 | 9.85 | 10.21 |
| $Co(ClO_4)_2\cdot TMPNO\cdot$ | Dark Green | 20.89 | 8841 | 4.58 | 26.11 | 25.85 | 4.38 | 4.68 | 3.38 | 3.03 | 14.23 | 14.57 |
| $Ni(ClO_4)_2\cdot TMPNO\cdot$ | Light green | 12.27 | 5267 | 3.53 | 26.11 | 26.22 | 4.38 | 4.71 | 3.38 | 3.07 | 14.19 | 14.38 |
| $Zn(ClO_4)_2\cdot 2TMPNO\cdot$ | Off-white | 2.58 | 1792 | 2.06 | 37.48 | 37.25 | 6.29 | 6.32 | 4.86 | 4.54 | 11.33 | 11.60 |

[a] $\chi_A^{corr}$ and $\mu_{eff}$ are, respectively, the corrected magnetic susceptibility and magnetic moment per metal atom.

**Table II.** Pertinent Infrared Data for TMPNO Metal Complexes (cm$^{-1}$).

| | Free TMPNO· [a] | $Fe(ClO_4)_2\cdot 2TMPNO\cdot$ | $Co(ClO_4)_2\cdot TMPNO\cdot$ | $Ni(ClO_4)_2\cdot TMPNO\cdot$ | $Zn(ClO_4)_2\cdot 2TMPNO$ |
|---|---|---|---|---|---|
| $\nu_{N-O}(\Delta\nu_{N-O})$ | 1339vs | 1292vs,b(—47) | 1296vs,b(—43) | 1298vs,b(—41) | 1305vs,b(—34) |
| Bands attributable to perchlorate vibrational modes | | 1218m-s<br>1122s<br>1088s<br>1041s<br>930s<br>919s,sh | 1204s,sh<br>1148s<br>1133s<br>1100s<br>1050s<br>1000s,sh<br>922s,b | 1202m-s<br>1140s<br>1107s,sh<br>1088s<br>1046s<br>998s,sh<br>925s,b | 1210m-s<br>1140vs<br>1091vs<br>1053vs<br>1018vs,sh<br>1000s,sh<br>931s<br>918s,sh |

[a] The IR spectrum of free TMPNO at 1300-850 cm$^{-1}$ exhibits the following bands: 1294w, 1260s, 1237vs, 1196m, 1171m, 1130m-s, 1082w, 1060w, 1040w, 975m, 951w, 930w, 895vw,b, 853w. Abbreviations: s: strong, m: medium, w: weak, v: very, b: broad, sh: shoulder.

**Table III.** Electronic Spectra of TMPNO· Metal Complexes.

| Compound | Medium | λ max, nm(ε max) |
|---|---|---|
| TMPNO· | Nujol<br>$1.6\times10^{-2}M$ in $(CH_3)_2CO—C_2H_5OH$ | 244vs, 310vs,sh, 464m-s<br>452(14.5) |
| $Fe(ClO_4)_2\cdot 2TMPNO\cdot$ | Nujol<br>In $(CH_3)_2CO—C_2H_5OH$ | 252vs, 348vs, 965sh, 1185m, 1325m,b<br>1130m, 1300m,b |
| $Co(ClO_4)_2\cdot TMPNO\cdot$ | Nujol<br>In $(CH_3)_2CO—C_2H_5OH$ | 259vs, 310s,sh, 592s, 634s, 745m, 815m-w,b, 1250w,vb<br>490s,sh, 945w, 1260m,b |
| $Ni(ClO_4)_2\cdot TMPNO\cdot$ | Nujol<br>$4\times10^{-3}M$ in $(CH_3)_2CO—C_2H_5OH$ | 256vs, 278s,sh, 378s, 650m, 760m,sh, 960w, 1290vw,vb<br>379(21), 700(13), 795sh, 990(8), 1323(4) |
| $Zn(ClO_4)_2\cdot 2TMPNO\cdot$ | Nujol<br>In $(CH_3)_2CO—C_2H_5OH$ | 260vs, 275vs,sh, 325vs, 420m-s,sh<br>345vs |

Abbreviations: s: strong, m: medium, w: weak, v: very, b: broad, sh: shoulder.

**Table IV.** Solid-State esr Spectra of TMPNO· and its Metal Complexes (107°K).

| Compound | $g_0$ | $g_1$ | $g_2$ | $g_3$ | $g_3$-$g_1$ |
|---|---|---|---|---|---|
| TMPNO· | 2.006 [a] | | | | |
| $Fe(ClO_4)_2\cdot 2TMPNO\cdot$ | | 1.946 | 2.004 | 2.050 | 0.104 |
| $Co(ClO_4)_2\cdot TMPNO\cdot$ | | 1.944 | 2.003 | 2.052 | 0.108 |
| $Ni(ClO_4)_2\cdot TMPNO\cdot$ | | 1.946 | 2.003 | 2.052 | 0.106 |
| $Zn(ClO_4)_2\cdot 2TMPNO\cdot$ | | 1.937 | 2.000 | 2.056 | 0.120 |

[a] Ref. 19.

The new complexes are insoluble in many organic solvents, e.g.: nitromethane, acetonitrile, *p*-dioxane, *o*-bromobenzene, ethyl acetate. The $Ni^{II}$ complex dissolves in a 1:1 acetone-ethanol mixture, while the other complexes are only sparingly soluble in this medium. Infrared (Table II) and electronic (Table III, Figure 1) spectra, and magnetic susceptibility (Table I) and molar conductance measurements were obtained by procedures described elsewhere.[17] $10^{-3}M$ solutions of the new complexes in 1:1 acetone-ethanol exhibit $\Lambda_M$ values ranging between 118 and 125 $\Omega^{-1}$ $cm^2$ $mole^{-1}$ at 25°C. Solid-state (Table IV, Figure 2) and solution esr spectra of the free radical and its metal complexes were obtained by using a Varian E-3 spectrometer with a modulation frequency of 100 KHz.

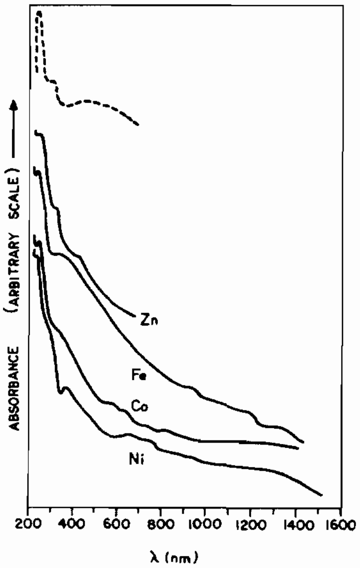

Figure 1. Solid-state (Nujol mull) uv-visible spectra of: (—) TMPNO· metal complexes; (---), uncomplexed TMPNO·.

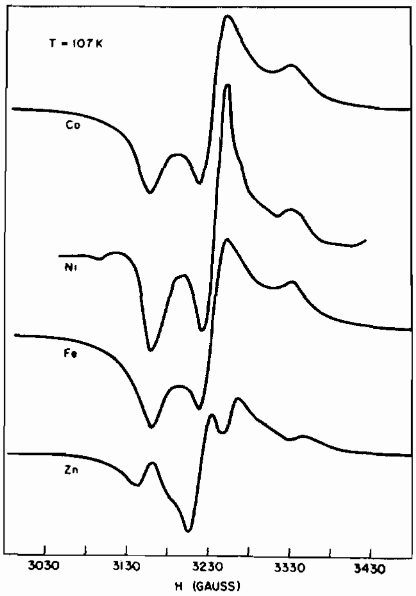

Figure 2. Solid-state esr spectra of TMPNO· metal complexes of 107°K.

## Discussion

*Background.* Adduct formation between nitroxide free radicals and metal salts differs from the normal Lewis base-Lewis acid interactions in that the base contains an unpaired electron. The possibility of interaction of an unoccupied orbital of the metal salt with the three π-electron fragment N---O of nitroxide free radicals has been advanced.[8] However, coordination through the N-O oxygen appears to be more probable; in fact, negative $\nu_{N\text{-}O}$ frequency shifts upon metal complex formation,[5,6] and increased nitrogen hyperfine splittings (relative to the splittings in the uncomplexed free radical) in the esr spectra of nitroxide free radical adducts with salts of diamagnetic metal ions,[7] or hydrogen-bonding acids,[18] as well as the protonated TMPNO·,[19] are strongly in favor of coordination to a ligand molecular orbital, which is largely a lone-pair oxygen orbital.

Interactions of nitroxide free radicals with diamagnetic metal ions, containing high percentages of isotopes with magnetic nuclei (i.e., $^{27}Al$, $^{69}Ga$, $^{71}Ga$), result in multi-line solution esr spectra, which are due to splittings of the three $^{14}N$ lines, appearing in the spectrum of the uncomplexed free radical,[15] under the influence of these nuclei.[7,8] No esr data for $Zn^{II}$ complexes with nitroxide free radicals have been reported; in complexes of zinc with nitrogen-containing free radicals, such as the flavin radical $Zn^{II}$ chelates, splittings of the $^{14}N$ lines due to interactions with the nucleus of the only magnetic Zn isotope ($^{67}Zn$) occur, but are generally difficult to observe, because of the low abundance (4.11% in naturally occurring zinc[20]) of this isotope.[21] In the spectra of $^{67}Zn$-enriched samples, these splittings are quite clearcut.[21] On the other hand, interactions between the spin of the unpaired electron of nitroxide free radicals and those of the unpaired d electrons of paramagnetic transition metal ions occur during reactions of nitroxide radicals with paramagnetic metallic compounds.[5,10-12] The solid state esr spectra of radicals of this type consist of one broad peak; this peak is resolved into three components when the free radical is oriented in crystals of a host-lattice (e.g., tetramethyl-1, 3-cyclobutanedione).[22] The solid-state esr spectra of tetrahedral complexes of the type $[Co(DTBNO\cdot)_2X_2]$ (X=Cl, Br, I)[5,12] are quite unusual for tetrahedral $Co^{II}$ complexes.[12] These spectra are typical of polycrystalline specimen with an anisotropic g-tensor. Beck *et al.* assumed that S = ½ and assigned three components to the g-tensor; $\mu_{eff}$ values determined by this group were *ca.* 2.7 BM.[5] However, a more recent magnetic susceptibility determination for $[Co(DTBNO\cdot)_2Br_2]$ led to a $\mu_{eff}$ value of 4.23 BM;[12] this value is indicative of interaction between the three unpaired electrons of high-spin $Co^{II}$ and the unpaired electron in each ligand, but rules out a S = ½ situation.[12] Cobalt

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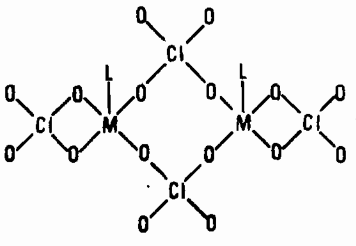
retains its +2 oxidation state in these complexes, as demonstrated by their electronic spectra, which are characteristic of $T_d$ Co$^{II}$.[5,12] Solution esr spectra of nitroxide free radical complexes with paramagnetic 3d metal ions are characterized by broadening and enhancement of the intensity of the three $^{14}$N esr peaks of the uncomplexed free radical.[5,10,11]

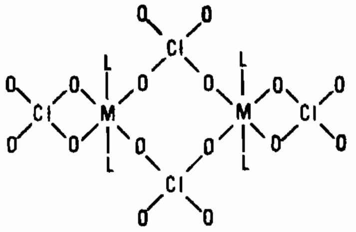
*Characterization of the new metal complexes.* The infrared spectra of the TMPNO· metal complexes (Nujol mulls, 4000-700 cm$^{-1}$, Table II) are characterized by negative $\nu_{N-O}$ shifts, which are suggestive of coordination of the ligand through the N-O oxygen. Coordinated water bands are generally absent from these spectra. The presence of coordinated perchlorato ligands is manifested by splittings of the $\nu_3$ mode of ionic $ClO_4^-$ and the fact that $\nu_1(ClO_4)$ is ir-active[23] (Table II). Multiple splittings in the $\nu_3(ClO_4)$ region (1220-990 cm$^{-1}$) and the occurrence of a split or broad $\nu_1(ClO_4)$ absorption (Table II), are indicative of the presence of two types of coordinated perchlorate in the new complexes. The high conductance values observed in acetone-ethanol solutions (*vide supra*) are presumably due to the displacement of coordinated perchlorato ligands by solvent molecules.

The visible n-π* transition of the free ligand[24] is masked in the spectra of the paramagnetic metal ion complexes. In the spectrum of the Zn$^{II}$ complex, it shows a blue shift, as would be expected[19,24,25] (Table III, Figure 1). The solid-state (Nujol mull) electronic spectra of the new complexes (Figure 1) are generally poorly resolved and cannot be, therefore, used for making unambiguous structural assignments. The Fe and Ni complexes show practically similar solid-state and solution electronic spectra (Table III). The solution spectra of these complexes suggest that the metal ions are in the +2 oxidation state, as would be expected,[5,12] and may be attributed to either hexa- or penta-coordinated structures. The solution spectrum of the Co complex is typical of hexacoordinated Co$^{II}$ compounds,[26] and substantially differs from the corresponding solid state spectrum (Table III). The latter spectrum may be indicative of coordination number five for the Co$^{II}$ ion (pentacoordinated aromatic amine N-oxide-Co$^{II}$ complexes exhibit (d-d) bands of medium intensity at 700-850 nm[26]). Finally, the solubility characteristics of the new complexes may be attributed to bi- or poly-nuclear structures. On the basis of the above discussion, structures of two types would seem as probable for the TMPNO· complexes, *viz.*: 1) bi- or poly-nuclear, TMPNO·-bridged, involving both mono- and bi-dentate perchlorato terminal ligands; 2) bi- or poly-nuclear, perchlorato-bridged, containing terminal TMPNO· and bidentate perchlorato ligands (the presence of ir bands at 1218-1202 cm$^{-1}$ is in favor of the presence of bidentate perchlorate[23]). Although heterocyclic amine N-oxides may act as bridging ligands,[27] the former possibility would be rather remote, in view of the severe steric hindrance introduced by the presence of four methyl substituents in the 2- and 6-ring positions of TMPNO·. Thus, structures of the types (II) and (III) are more probable for the 1:1 and 2:1 complexes, respectively (L = TMPNO·); these binuclear structures involve pentacoordination for Co$^{II}$ and Ni$^{II}$ and hexacoordination for Fe$^{II}$ and Zn$^{II}$. Linear polynuclear structures of the same general types (i.e., $(O_2ClO_2)M(L)_n[(O_2ClO_2)_2M(L)_n]_x(O_2ClO_2)_2M(L)_n(O_2ClO_2)$, where x = 1, 2, 3... and n = 1 or 2) are also possible.



(M = Co, Ni)

(II)



(M = Fe, Zn)

(III)

The magnetic susceptibility data for the new complexes are generally suggestive of spin-spin interactions. In the case of the Zn$^{II}$ complex a $\mu_{eff}$ value of 2.44 BM (i.e., $\sqrt{2(1.73)^2}$) per monomeric unit would be expected, if no interaction between the unpaired electrons of the two TMPNO· ligands occurred.[28] The $\mu_{eff}$ observed for this complex (2.06 BM; Table I) is thus, suggestive of intra-molecular spin-pairing.[28] For the paramagnetic metal ion complexes, the lowest possible $\mu_{eff}$ values per metal atom would be as follows, if no interaction between the unpaired d electrons of the metal ion and the unpaired electron(s) of the ligand(s) occurred:[12] Fe$^{II}$ complex $\mu_{eff} = \sqrt{(4.9^2 + 2(1.73)^2} = 5.47$ BM; Co$^{II}$ complex: $\mu_{eff} = \sqrt{(4.45)^2 + (1.73)^2} = 4.79$ BM; Ni$^{II}$ complex: $\mu_{eff} = \sqrt{(3.10)^2 + (1.73)^2} = 3.69$ BM. The μ values utilized for the metal ions in the above calculations are among the lowest reported for high-spin hexacoordinated Fe$^{II}$ [29] and pentacoordinated Co$^{II}$ and Ni$^{II}$ [30] compounds; hence, the $\mu_{eff}$ of the new complexes would most probably be substantially higher than the values calculated above, should no spin-spin interaction of any kind occur. The observed magnetic moments

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(Table I) are generally lower than the calculated $\mu_{eff}$, and indicate that interactions between the unpaired metal ion and ligand electrons do occur. The $Fe^{II}$ complex exhibits a $\mu_{eff}$ characteristic of $d^6$ compounds exhibiting a half-quenched spin.[17] It would, therefore, appear that two of the unpaired d electrons of the metal ion are paired with the unpaired electrons of the two ligand groups. In the $Co^{II}$ and $Ni^{II}$ complexes, the coupling between unpaired metal ion d electrons and the unpaired electron of the ligand, is apparently only partial.

Acetone-ethanol solution esr spectra of the new complexes are very similar to those of the uncomplexed free radical in solution, i.e., they exhibit three equally spaced, equally intense lines, which are characteristic of a single unpaired electron interacting with a single nitrogen nucleus.[5,15,24,25] The solid-state esr spectra of the four new complexes (Table IV, Figure 2) are very similar to one another. These spectra, which exhibit anisotropic g-values, show similarities to those reported for transition metal ion complexes with various nitrogen-containing "suspect" ligands.[31,32] The g-value anisotropy is too large for a nitroxide free radical species, with the unpaired electron localized largely on nitrogen, as is the case with TMPNO$\cdot$[33] (e.g., anisotropic g-values for DTBNO$\cdot$: 2.00270, 2.00616, 2.00872;[22] and for the iminoxy radical $CH_3C = (NOH)C = (\dot{N}O)CH_3$: 2.0026, 2.0063, 2.0095[34]). Moreover, the $g_3$-$g_1$ value[31] is apperently metal sensitive, decreasing along the series $Zn > Co > Ni > Fe$, while the intensity of the peaks decreases in the order $Fe \sim Co > Ni > Zn$. The spectra of the paramagnetic metal ions are generally unusual for $3d^{6-8}$ compounds.[12,35] On the other hand, the similarity of the esr spectra of the paramagnetic metal ion complexes to that of the $Zn^{II}$ complex suggests that they are largely due to the unpaired electron associated with TMPNO$\cdot$, and the anisotropy observed probably arises from intramolecular interactions between the $^{14}N$ nuclei and the unpaired ligand- and, in the case of the paramagnetic metal ions, d-electrons present in the dimeric complex molecules.[28,31,32] Spin-pairing between two unpaired d-electrons of high-spin $Fe^{II}$ and the two unpaired electrons of the two ligand molecules, suggested by the $\mu_{eff}$ of the $Fe^{II}$ complex (*vide supra*) is therefore, unlikely. An alternative possibility is that $Fe^{II}$ is partially spin-paired, as for instance in the case of certain complexes with chelating nitrogen ligands[36] or 2,6-lutidine N-oxide,[17] and there is only partial interaction between the two unpaired ligand and the two unpaired d electrons.

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