

Radical Superexchange in Semiquinone Complexes Containing Diamagnetic Metal Ions. 3,6-Di-*tert*-butyl-1,2-semiquinone Complexes of Zinc(II), Cobalt(III), Gallium(III), and Aluminum(III)

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The tris(3,6-di-*tert*-butylsemiquinonato)gallium(III), -aluminum(III), and -cobalt(III) complexes have been studied structurally, spectrally, and magnetically. Complexes of the three diamagnetic metals have octahedral structures of D_3 symmetry ($\text{Ga}(3,6\text{-DBSQ})_3$, monoclinic, $C2/c$, $a = 22.069(6)$ Å, $b = 19.365(5)$ Å, $c = 10.163(3)$ Å, $\beta = 94.90(2)^\circ$, $V = 4327(2)$ Å³, $Z = 4$; $\text{Co}(3,6\text{-DBSQ})_3$, monoclinic, $C2/c$, $a = 21.799(6)$ Å, $b = 19.376(8)$ Å, $c = 10.167(3)$ Å, $\beta = 94.99(3)^\circ$, $V = 4278(3)$ Å³, $Z = 4$). EPR spectra recorded on $\text{Ga}(3,6\text{-DBSQ})_3$ and $\text{Al}(3,6\text{-DBSQ})_3$ in a toluene glass at 77 K show signals at g values of 2, 4, and 6, indicative of a $S = 3/2$ ground state. Variable-temperature magnetic measurements show an increase in magnetic moment below 70 K from $3.0 \mu_B$, the value expected for three noninteracting $S = 1/2$ radicals, toward the $3.8 \mu_B$ value for a $S = 3/2$ ferromagnetically coupled ground state. This behavior has been fit to a theoretical model with J values of 6.2 and 8.6 cm^{-1} for the Ga and Al complexes, respectively. EPR spectra recorded on $\text{Co}(3,6\text{-DBSQ})_3$ show evidence for a $S = 1/2$ ground state at temperatures below 77 K and magnetic moment decreases at low temperature consistent with an antiferromagnetically coupled doublet ground state ($J = -39.1 \text{ cm}^{-1}$). The zinc(II) complex $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ has been prepared and fully characterized ($\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$, monoclinic, $P2_1/c$, $a = 17.157(5)$ Å, $b = 11.563(3)$ Å, $c = 19.864(4)$ Å, $\beta = 113.26(2)^\circ$, $V = 3620(1)$ Å³, $Z = 4$). The monomeric complex shows an EPR spectrum at 77 K with a zero-field-split $\Delta M_S = 1$ transition and a half-field $\Delta M_S = 2$ transition from a $S = 1$ spin state. Magnetic measurements indicate that the complex has a diamagnetic singlet ground state ($J = -33.7 \text{ cm}^{-1}$) and that EPR activity results from thermal population of the triplet state that lies 67.4 cm^{-1} above the singlet. The difference in the exchange interaction between radical ligands bonded to the Al and Ga metal ions relative to Co and Zn appears related to d-orbital participation in metal-SQ π bonding. The mixed-charge ligand complex $\text{Ga}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ has been prepared to study the possibility of interligand electron transfer. The complex shows no band that may be assigned as an interligand intervalence-transfer transition, but the EPR spectrum of the complex recorded in solution at 210 K shows a pattern of hyperfine coupling that is consistent with time-averaged quinone ligands.

Introduction

Studies on the preparation of magnetic organic materials have stimulated theoretical investigations on the nature of interacting organic radicals in bulk polymers and presented a considerable challenge to researchers attempting to synthesize materials that show cooperative magnetic effects.¹ Control of spin alignment between radical subunits is of fundamental importance, and the link between paramagnetic centers often defines the nature of radical coupling. Many of the most stable organic radicals have oxygen and/or nitrogen functionalities that may coordinate with metal ions, and the coordination chemistry of organic radicals has developed rapidly with interest in materials that show unique magnetic effects that result from the combined interactions between radicals and paramagnetic metal ions.²

It is possible to use a diamagnetic metal ion as a linking agent between organic radicals in systems where the electronic structure of the metal ion bridge provides an orbital pathway for interradical exchange. For example, antiferromagnetic exchange between *tert*-butyl-substituted semiquinone ligands chelated to square planar metals of the Ni(II), Pd(II), Pt(II) series in the neutral $\text{M}(\text{SQ})_2$ complexes is strong and results in compounds that are either diamagnetic or weakly paramagnetic.³ Parameters that define the nature of exchange are less clearly defined for metal

complexes than for molecules consisting of conjugated organic bridges of reasonably well-defined orbital composition. In this report we present studies on octahedral complexes containing radical semiquinone ligands linked by chelation to diamagnetic metal ions. The results of these studies demonstrate the dependence of the exchange interaction upon metal ion configuration.

Experimental Section

Materials. *N,N,N',N'*-Tetramethylethylenediamine (tmeda) was purchased from Aldrich. Dicobalt octacarbonyl and nickel tetracarbonyl were purchased from Strem Chemical Co. 3,6-Di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ),⁴ thallium 3,6-di-*tert*-butyl-1,2-semiquinone ($\text{Tl}(3,6\text{-DBSQ})$), and thallium 3,6-di-*tert*-butylcatecholate ($\text{Tl}_2(3,6\text{-DBCat})$)⁵ were prepared using literature procedures.

Complex Syntheses. $\text{Ga}(3,6\text{-DBSQ})_3$. GaI_3 (155 mg, 0.344 mmol) and $\text{Tl}(3,6\text{-DBSQ})$ (410 mg, 0.964 mmol) were dissolved in 50 mL of toluene. The yellow precipitate of TII was separated from the mixture by filtration, and the filtrate was slowly evaporated to give emerald green crystals of $\text{Ga}(3,6\text{-DBSQ})_3$ in 85% yield.

$\text{Al}(3,6\text{-DBSQ})_3$. AlCl_3 (56 mg, 0.42 mmol) and $\text{Tl}(3,6\text{-DBSQ})$ (527 mg, 1.24 mmol) were dissolved in 50 mL of toluene. The white precipitate

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(2) (a) Cogne, A.; Grand, A.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* 1989, 111, 3230. (b) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* 1993, 261, 447.

(3) (a) Fox, G. A.; Pierpont, C. G. *Inorg. Chem.* 1992, 31, 3718. (b) Abakumov, G. A.; Cherkasov, V. K.; Bubnov, M. P.; Ellert, O. G.; Rakitin, U. V.; Zakharov, L. N.; Struchkov, Y. T.; Safyanov, U. N. *Izv. Akad. Nauk SSSR* 1992, 2315.
(4) Belostotskaya, I. S.; Komissarova, N. L.; Dzhuaryan, E. V.; Ershov, V. V. *Izv. Akad. Nauk SSSR* 1984, 1610.
(5) Muraev, V. A.; Abakumov, G. A.; Razuvaev, G. A. *Dokl. Akad. Nauk SSSR* 1974, 217, 1083.

Table 1. Crystallographic Data for Ga(3,6-DBSQ)₃, Co(3,6-DBSQ)₃, and Zn(tmEDA)(3,6-DBSQ)₂^a

	Ga(3,6-DBSQ) ₃	Co(3,6-DBSQ) ₃	Zn(tmEDA)- (3,6-DBSQ) ₂
mol wt	730.6	719.8	622.2
color	green	blue	blue
crystal system	monoclinic	monoclinic	monoclinic
space group	C2/c	C2/c	P2 ₁ /c
a (Å)	22.069(6)	21.799(6)	17.157(5)
b (Å)	19.365(5)	19.376(8)	11.563(3)
c (Å)	10.163(3)	10.167(3)	19.864(4)
β (deg)	94.90(2)	94.99(3)	113.26(2)
V (Å ³)	4327(2)	4278(3)	3620.4(15)
Z	4	4	4
D _{calc} (g cm ⁻³)	1.12	1.12	1.14
μ (mm ⁻¹)	0.671	0.438	0.727
R, R _w ^b	0.071, 0.079	0.035, 0.042	0.068, 0.059
GO ^c	1.54	1.38	1.20

^a Radiation Mo Kα (0.710 73 Å); T = 293–298 K. ^b R = ∑||F_o| - |F_c||/∑|F_o|; R_w = [∑w(|F_o| - |F_c||)²/∑w(F_o)²]^{1/2}.

of TiCl₃ was separated from the mixture by filtration, and the filtrate was slowly evaporated to give emerald green crystals of Al(3,6-DBSQ)₃ in 87% yield.

Co(3,6-DBSQ)₃. Co₂(CO)₈ (68 mg, 0.20 mmol) and 3,6-DBBQ (248 mg, 1.13 mmol) were dissolved in 35 mL of a 1:1 hexane-dichloromethane solution under N₂. The color of the solution turned to a deep blue, and the mixture was stirred for 24 h at room temperature. The volume of the solution was then reduced, giving Co(3,6-DBSQ)₃ as dark blue crystals in 66% yield.

Ga(tmEDA)(3,6-DBSQ)(3,6-DBCat). A 30-mL toluene solution of Ti₂(3,6-DBCat) was prepared by warming 3,6-DBBQ (147 mg, 0.667 mmol) over thallium amalgam. The solution was transferred to a second flask containing additional 3,6-DBBQ (49 mg, 0.222 mmol) to give a 1:1 mixture of Ti(3,6-DBSQ) and Ti₂(3,6-DBCat). This solution was combined with GaI₃ (201 mg, 0.446 mmol) and tmEDA (250 mg, 0.215 mmol) dissolved in 10 mL of toluene. A yellow precipitate of TiI₂ formed and was separated from the mixture by filtration. Evaporation of the filtrate gave green microcrystals of Ga(tmEDA)(3,6-DBSQ)(3,6-DBCat) in 11% yield.

Zn(tmEDA)(3,6-DBSQ)₂. A solution containing 3,6-DBBQ (256 mg, 1.16 mmol) and tmEDA (0.5 mL, 3 mmol) dissolved in 20 mL of toluene was added to 0.5 g of mossy zinc and 1.0 mL of mercury under N₂. The mixture was heated for 6 h to give a blue solution of the complex. The solution was separated from the solid residue and condensed in volume to give dark blue crystals of Zn(tmEDA)(3,6-DBSQ)₂ in 72% yield.

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic measurements were made using a Quantum Design SQUID magnetometer at a field strength of 5 kG. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR with samples prepared as KBr pellets. EPR spectra were recorded on a Bruker ESP-300E and referenced to DPPH as the g value standard.

Crystallographic Structure Determinations. Ga(3,6-DBSQ)₃. Emerald green crystals of the complex were grown by slow evaporation of a toluene solution. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 intense reflections with 2θ values between 18 and 26° gave the unit cell dimensions listed in Table 1. Data were collected by θ-2θ scans within the angular range 3.0–45°. Density measurements indicated that there were four molecules per unit cell, and a Patterson map was used to locate the Ga atom at a position of crystallographic 2-fold symmetry. Phases generated from the Ga location gave the positions of other non-hydrogen atoms of the molecule. Final cycles of refinement converged with discrepancy indices of R = 0.071 and R_w = 0.079. Table 2 contains the positions of selected atoms of the molecule; tables containing a full listing of atom positions, anisotropic displacement parameters, and hydrogen atom locations are available as supplementary material.

Axial photographs with scans on related reflections were used to verify that crystals of Al(3,6-DBSQ)₃ were isostructural with crystals of Ga(3,6-DBSQ)₃.

Co(3,6-DBSQ)₃. Dark blue crystals of the complex were grown by slow evaporation of a hexane-dichloromethane solution. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 intense reflections with 2θ values between 9 and 36° gave the unit cell dimensions listed in Table 1. Data were collected by θ-2θ scans within the angular range 3.0–45°. Unit cell dimensions and reflection intensities indicated that the cobalt complex was isostructural with the gallium

Table 2. Selected Atom Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Ga(3,6-DBSQ)₃

	x/a	y/b	z/c	U _{eq} ^a
Ga	0	2740(1)	2500	48(1)
O1	478(2)	2762(3)	4200(5)	49(2)
O2	608(3)	3403(3)	2053(6)	50(2)
C1	977(4)	3090(4)	4185(8)	38(3)
C2	1039(4)	3473(4)	2928(8)	40(3)
C3	1570(4)	3886(4)	2823(8)	43(3)
C4	1994(4)	3869(5)	3828(10)	57(4)
C5	1951(4)	3467(5)	5005(10)	59(4)
C6	1450(4)	3087(4)	5197(8)	48(3)
O3	493(2)	1970(3)	1880(6)	51(2)
C15	265(3)	1375(4)	2137(8)	44(3)
C16	555(4)	756(5)	1772(8)	47(3)
C17	258(4)	171(5)	2135(9)	60(4)

^a U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Atom Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Co(3,6-DBSQ)₃

	x/a	y/b	z/c	U _{eq} ^a
Co	0	2687(1)	2500	42(1)
O1	-554(1)	3362(1)	2991(2)	46(1)
O2	-459(1)	2690(1)	854(2)	46(1)
C1	-1005(1)	3437(2)	2093(3)	39(1)
C2	-958(1)	3045(2)	892(3)	39(1)
C3	-1435(1)	3054(2)	-160(3)	41(1)
C4	-1919(2)	3466(2)	45(3)	52(1)
C5	-1957(2)	3867(2)	1206(3)	54(1)
C6	-1515(2)	3878(2)	2244(3)	45(1)
O3	504(1)	1981(1)	1938(2)	44(1)
C15	282(1)	1378(2)	2174(3)	38(1)
C16	560(1)	754(2)	1796(3)	41(1)
C17	271(1)	168(2)	2151(3)	54(1)

^a U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

complex. The solution to the gallium structure was used in initial refinements with the data obtained on crystals of the cobalt complex. Final cycles of refinement converged with discrepancy indices of R = 0.035 and R_w = 0.042. Table 3 contains the positions of selected atoms of the molecule; tables containing a full listing of atom positions, anisotropic displacement parameters, and hydrogen atom locations are available as supplementary material.

Zn(tmEDA)(3,6-DBSQ)₂. Dark blue crystals of the complex were grown by slow evaporation of an acetone solution. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 intense reflections with 2θ values between 20 and 32° gave the unit cell dimensions listed in Table 1. Data were collected by θ-2θ scans within the angular range 3.0–50°. Systematic absences were consistent with space group P2₁/c. The location of the Zn atom was determined from a Patterson map, and the locations of other non-hydrogen atoms were obtained using phases derived from the Zn atom location. Final cycles of refinement converged with discrepancy indices of R = 0.068 and R_w = 0.059. Table 4 contains the positions of selected atoms of the molecule; tables containing a full listing of atom positions, anisotropic displacement parameters, and hydrogen atom locations are available as supplementary material.

Results

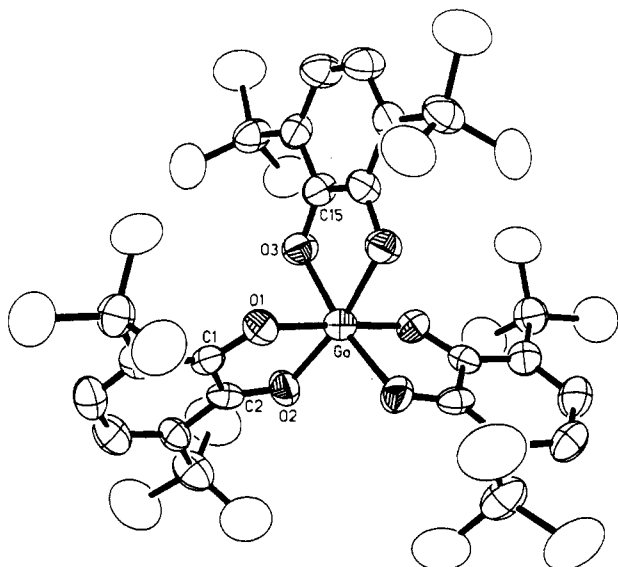
Diamagnetic metal ions may be used to form polyradical compounds by the coordination of radical donor atoms to the central metal. Our study has concerned the metal ion dependence of the interaction between chelated radicals for complexes prepared with transition metals and post transition metal ions. The 3,6-di-*tert*-butyl-1,2-semiquinone (3,6-DBSQ) ligand has been used in this investigation. The presence of large substituents at ring positions adjacent to the oxygen atoms suppresses formation of oligomeric products that have complicated synthetic reactions with 3,5-DBSQ and other semiquinone ligands containing exposed oxygen atoms available for bridging interactions.

Ga(3,6-DBSQ)₃. Two synthetic routes are available to Ga(3,6-DBSQ)₃. The complex may be formed by the direct reaction of amalgamated Ga metal with 3,6-DBBQ or by the procedure described in the Experimental Section that begins with GaI₃ and

Table 4. Selected Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^a
Zn	1671(1)	385(1)	2205(1)	48(1)
O1	2821(4)	308(6)	2098(3)	56(3)
O2	1534(4)	1704(6)	1452(3)	52(3)
C1	2977(6)	1221(10)	1836(5)	44(5)
C2	2262(7)	2031(9)	1468(5)	40(5)
C3	2378(7)	3108(9)	1175(5)	46(5)
C4	3186(8)	3329(9)	1250(5)	57(6)
C5	3886(6)	2570(9)	1594(5)	51(5)
C6	3802(7)	1539(9)	1884(5)	41(5)
O3	2169(4)	-629(5)	3138(3)	51(3)
O4	2114(4)	1629(6)	3026(4)	59(3)
C16	2650(7)	1206(8)	3612(6)	42(5)
C17	3239(7)	1889(8)	4194(6)	44(5)
C18	3792(6)	1311(9)	4787(6)	51(5)
C19	3793(7)	89(8)	4855(6)	55(5)
C20	3248(6)	-616(7)	4349(6)	39(5)
C21	3242(7)	3213(8)	4133(6)	46(5)
N1	366(5)	501(11)	2123(6)	81(5)
N2	1154(8)	-1069(9)	1446(6)	84(6)

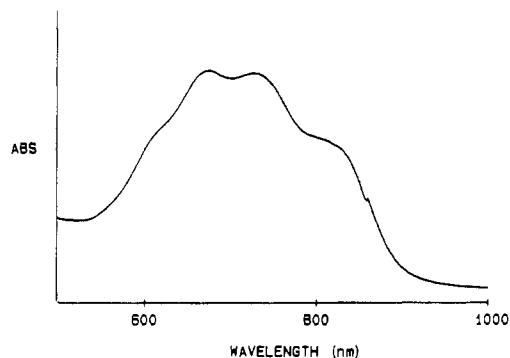
^a U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

**Figure 1.** View of the $\text{Ga}(3,6\text{-DBSQ})_3$ molecule.**Table 5.** Bond Lengths and Angles for $\text{Ga}(3,6\text{-DBSQ})_3$

Bond Lengths (\AA)				
Ga-O1	1.946(5)	Ga-O2	1.939(6)	
Ga-O3	1.981(6)	O1-C1	1.271(10)	
O2-C2	1.262(10)	C1-C2	1.494(12)	
C2-C3	1.430(12)	C3-C4	1.327(12)	
C4-C5	1.437(14)	C5-C6	1.355(13)	
C1-C6	1.402(11)	O3-C15	1.292(10)	
C15-C15'	1.437(16)	C15-C16	1.423(12)	
C16-C17	1.375(12)	C17-C17'	1.412(18)	
Angles (deg)				
O1-Ga-O2	81.9(2)	O3-Ga-O3'	82.3(3)	
[O1,O2',O3']/[O2,O3,O1'] twist				50.8

$\text{Ti}(3,6\text{-DBSQ})_6$. Structural characterization has shown that the complex molecule is octahedral with Ga-O lengths to the chelated oxygen donors that range from 1.939(6) to 1.981(6) \AA and average to 1.955 \AA . A view of the molecule is shown in Figure 1, and selected bond lengths and angles are given in Table 5. The average Ga-O length of $\text{Ga}(3,6\text{-DBSQ})_3$ is shorter than the corresponding length of *fac*- $\text{Ga}(3,5\text{-DBSQ})_3$, which is 1.978 \AA , and the average

(6) Prokof'ev, A. I.; Bubnov, N. N.; Solodovnikov, S. P.; Kabachnik, M. I. *Dokl. Akad. Nauk SSSR* 1979, 245, 178.

**Figure 2.** Electronic spectrum of the $[3,6\text{-DBSQ}]^-$ anion recorded in dichloromethane solution as the $[\text{CoCp}_2]^+$ salt.

Ga-O length of $[\text{Ga}(\text{Cat})_3]^{3-}$, 1.983 \AA .^{7,8} The twist angle of the trischelated octahedron of $\text{Ga}(3,6\text{-DBSQ})_3$ is 50.8°, comparing with values of 47.0° for $\text{Ga}(3,5\text{-DBSQ})_3$ and 48.8° for $[\text{Ga}(\text{Cat})_3]^{3-}$. Structural features of the semiquinone ligands are consistent with their charge. The average C-O length is 1.28(1) \AA , and the pattern of C-C lengths within the rings shows a slight contraction at the C3-C4 and C5-C6 bonds, positions that would be double bonds for the corresponding benzoquinone.⁹

Optical spectra recorded for the complex show three relatively intense transitions in the UV at 217 nm ($4600 \text{ M}^{-1} \text{ cm}^{-1}$), 299 (17 000), and 367 (3100) and a broad, structured transition with peaks at 720 (sh), 814 (930), 908 (930), and 1030 (sh). This spectrum and particularly the latter feature are quite similar to the spectrum of the free $[3,6\text{-DBSQ}]^-$ anion, shown in Figure 2. The optical spectrum of the semiquinone anion has been measured for a sample prepared by the stoichiometric addition of cobaltocene to 3,6-DBSQ in dichloromethane solution. Four transitions appear in the visible region as two overlapping bands at 673 nm (590) and 722 (580) with shoulders on the high- and low-energy sides at 612 and 811 nm. These bands have been attributed to semiquinone $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions,¹⁰ and the similarity between the spectra of the complex and free ligand show that the electronic structure of the ligand is only slightly perturbed upon coordination with Ga(III). The corresponding series of bands for $\text{Ga}(3,6\text{-DBSQ})_3$ is shifted by roughly 200 nm to lower energy.

At room temperature, $\text{Ga}(3,6\text{-DBSQ})_3$ in CDCl_3 solution shows a broad *tert*-butyl NMR resonance at 2.7 ppm (fwhm = 81 Hz) that sharpens at higher temperatures and broadens further as temperature is decreased. In toluene solution, an EPR spectrum develops over the temperature range that the NMR signal broadens. The solution spectrum consists of a single line centered at $g = 2.005$. In a solid toluene glass at 77 K, the spectrum obtained (Figure 3) consists of $\Delta M_S = 1, 2,$ and 3 transitions at g values of 2.003, 4.001, and 6.032, respectively. The $\Delta M_S = 1$ transition shows satellites associated with transitions between levels that arise from the effects of zero-field splitting with $D = 117 \times 10^{-4} \text{ cm}^{-1}$. The central resonance shows addition coupling of 7.4 G to the $I = 3/2$ isotopes of Ga (^{69}Ga (60.2%), ^{71}Ga (39.8%)), and hyperfine lines can also be seen on the $\Delta M_S = 2$ transition. This spectrum is similar to the spectrum reported for $\text{Ga}(3,6\text{-DBSQ})_3$ by Prokof'ev and Solodovnikov⁶ and similar to the spectrum of $\text{Ga}(3,5\text{-DBSQ})_3$ reported by McGarvey.^{7a} It arises from the $S = 3/2$ magnetic ground state for the complex at 77

- (7) (a) Ozarowski, A.; McGarvey, B. R.; El-Hadad, A.; Tian, Z.; Tuck, D. G.; Krovich, D. J.; DeFotis, G. C. *Inorg. Chem.* 1993, 32, 841. (b) Adams, D. M.; Rheingold, A. L.; Dei, A.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 391.
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- (9) (a) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* 1981, 38, 45. (b) Carugo, O.; Castellani, C. B.; Djinovic, K.; Rizzi, M. *J. Chem. Soc., Dalton Trans.* 1992, 837.
- (10) Hobza, P.; Carsky, P.; Zahradnik, R. *Collect. Czech. Chem. Commun.* 1973, 38, 641.

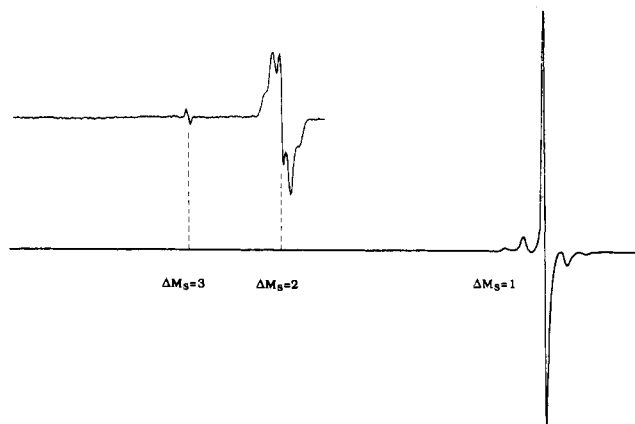


Figure 3. EPR spectrum of Ga(3,6-DBSQ)₃ recorded in toluene glass at 77 K.

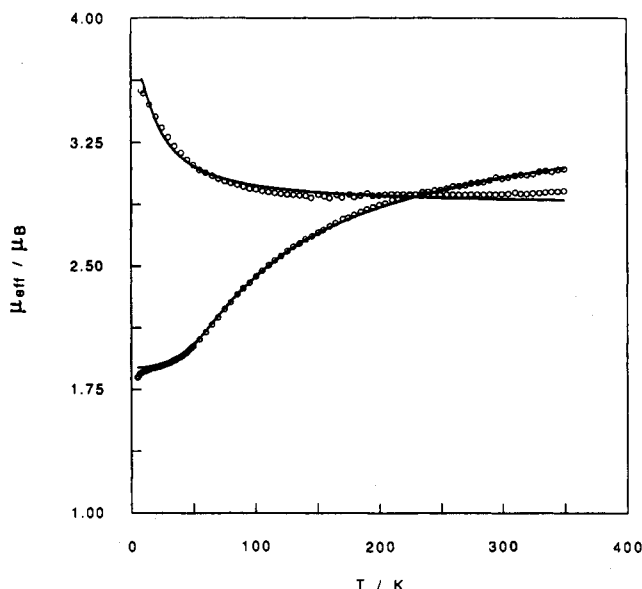


Figure 4. Plots of effective magnetic moment vs temperature for Ga(3,6-DBSQ)₃ and Co(3,6-DBSQ)₃. The solid lines show the theoretical fit of $J_{SQ,SQ} = 6.2 \text{ cm}^{-1}$ for Ga(3,6-DBSQ)₃ and $J_{SQ,SQ} = -39.1 \text{ cm}^{-1}$ for Co(3,6-DBSQ)₃.

K that results from ferromagnetic coupling between the three $S = 1/2$ radical ligands.

The results of magnetic measurements made on Ga(3,6-DBSQ)₃ over the temperature range 350–5 K are shown in Figure 4. Above 70 K, the complex exhibits a magnetic moment near the value of $3.0 \mu_B$ expected for three noninteracting $S = 1/2$ centers. Below this temperature, the magnetic moment increases to $3.62 \mu_B$ at 5 K, approaching the $3.87 \mu_B$ value expected for the ferromagnetically coupled $S = 3/2$ magnetic ground state. This temperature dependence has been modeled to give the result shown as the solid line in Figure 4 with $J = 6.23 \text{ cm}^{-1}$ for $g = 1.91$.¹¹ These values are in agreement with $J = 7.8 \text{ cm}^{-1}$ and $g = 1.92$ obtained by Hendrickson from the theoretical fit to temperature-dependent magnetic measurements made on Ga(3,5-DBSQ)₃.^{7b}

Al(3,6-DBSQ)₃. The reaction between AlCl₃ and Ti(3,6-DBSQ) has been used to form Al(3,6-DBSQ)₃. Prokof'ev had prepared the complex earlier by treating Al amalgam with 3,6-DBBQ and reported its EPR spectrum.⁶ Crystals of the complex are emerald green, and intensity measurements on selected reflections have indicated that the complex is isostructural with Ga(3,6-DBSQ)₃. Its infrared spectrum is identical to the spectrum of the gallium analog as is the electronic spectrum of the complex. EPR spectra recorded in toluene glass at 77 K show $\Delta M_S = 1, 2,$ and 3 transitions with satellites resulting from zero-field splittings on the $\Delta M_S = 1$ signal ($D = 132 \times 10^{-4} \text{ cm}^{-1}$). On this

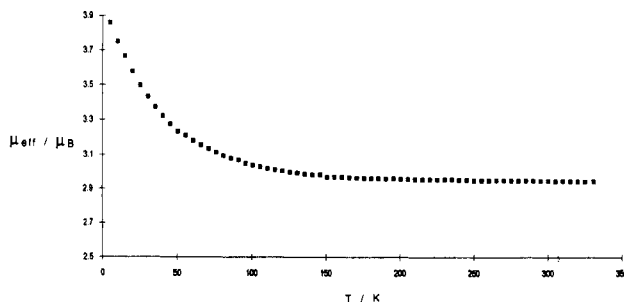


Figure 5. Plot of effective magnetic moment vs temperature for Al(3,6-DBSQ)₃.

basis, the complex has been assumed to have a $S = 3/2$ ground state with interradical coupling that is similar to that of its Ga analog. The results of magnetic measurements carried out on the complex are shown in Figure 5. At temperatures above 100 K, the magnetic moment remains near the $3.0 \mu_B$ value expected for three noninteracting radicals. Near 100 K, the magnetic moment begins to increase to $3.86 \mu_B$ at 5 K, a value that is consistent with the $S = 3/2$ ferromagnetically coupled ground state for the complex. The temperature dependence has been fit to the theoretical expression used for Ga(3,6-DBSQ)₃, giving a value for J of 8.55 cm^{-1} for $g = 1.93$.

Co(3,6-DBSQ)₃. The reaction between Co₂(CO)₈ and 3,6-DBBQ cleanly gives Co(3,6-DBSQ)₃. This result is different from the related reaction carried out with 3,5-DBBQ where the [Co(3,5-DBSQ)₂]₄ tetramer containing Co(II) was obtained.¹² The oxygen atom bound at the ring 1-position of 3,5-DBBQ is exposed, and it is frequently found to bridge metal ions in dimeric and oligomeric complexes. Bridging interactions of this type are responsible for the tetrameric structure of [Co(3,5-DBSQ)₂]₄, and the difference in chemistry between 3,6-DBBQ and 3,5-DBBQ in their reactions with Co₂(CO)₈ illustrates the advantage of using 3,6-DBBQ to give simple chelated complexes. In the solid state, Co(3,6-DBSQ)₃ is air stable, but in solution, the complex slowly decomposes with dissociation of 3,6-DBBQ. The infrared spectrum is similar to spectra obtained on Ga(3,6-DBSQ)₃ and Al(3,6-DBSQ)₃, and the electronic spectrum shows transitions at 302 nm ($9200 \text{ M}^{-1} \text{ cm}^{-1}$) and 399 (4200) and the structured four-component series of low-energy transitions centered about 916 nm ($1500 \text{ M}^{-1} \text{ cm}^{-1}$) that appear characteristically for the semiquinone complexes of Ga and Al. Transitions that appear to involve metal levels, which are not present in the spectra of the Ga and Al complexes, occur at 516 nm (2000) and as a broad transition of low intensity that is centered about 1650 nm.

Crystals of Co(3,6-DBSQ)₃ obtained by slow evaporation of the solution used for the reaction have been studied crystallographically. The complex molecule is isostructural with Ga(3,6-DBSQ)₃, as shown in Figure 6. Selected bond lengths and angles are given in Table 6. The average Co–O bond length of 1.876 \AA is characteristic of low-spin Co(III) and 0.2 \AA shorter than values to the high-spin Co(II) ions of [Co(3,5-DBSQ)₂]₄.¹² The twist angle of 56.5° is close to the 60° value of a regular

- (11) The temperature dependence of magnetic susceptibility was modeled using the Kambe expression for trimers exhibiting isotropic exchange:

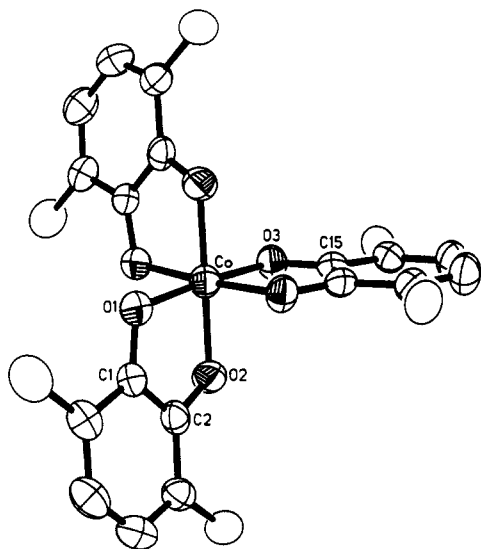
$$H = -2J_{SQ,SQ}(S_1S_2 + S_1S_3 + S_2S_3)$$

$$\chi_M = (Ng^2\beta^2/4kT)[(1 + 5e^x)/(1 + e^x)] + \text{TIP}$$

$$x = 3J_{SQ,SQ}/kT$$

A nonlinear regression analysis was used to fit the experimental data. For Ga(3,6-DBSQ)₃, theoretical values of $J_{SQ,SQ} = 6.2 \text{ cm}^{-1}$, $g = 1.91$, TIP = 0 provided the best fit. For Al(3,6-DBSQ)₃, values of $J_{SQ,SQ} = 8.6 \text{ cm}^{-1}$, $g = 1.93$, TIP = 0 were used. Values of $J_{SQ,SQ} = -39.1 \text{ cm}^{-1}$, $g = 2.17$, TIP = $2.36 \times 10^{-4} \text{ emu/mol}$ gave the best fit for Co(3,6-DBSQ)₃.

- (12) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439.

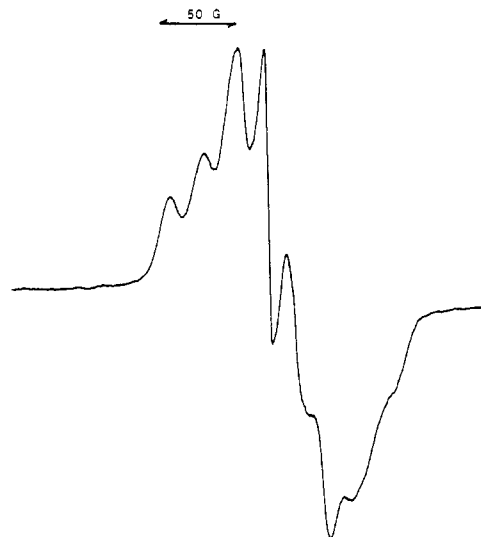
Figure 6. View of the $\text{Co}(3,6\text{-DBSQ})_3$ molecule.Table 6. Bond Lengths and Angles for $\text{Co}(3,6\text{-DBSQ})_3$

Bond Lengths (Å)			
Co-O1	1.878(2)	Co-O2	1.874(2)
Co-O3	1.875(2)	O1-C1	1.290(4)
O2-C2	1.291(4)	C1-C2	1.449(4)
C2-C3	1.424(4)	C3-C4	1.355(5)
C4-C5	1.420(5)	C5-C6	1.365(5)
C1-C6	1.422(4)	O3-C15	1.294(4)
C15-C15'	1.449(6)	C15-C16	1.420(4)
C16-C17	1.362(4)	C17-C17'	1.430(7)
Angles (deg)			
O1-Co-O2	86.0(1)	O3-Co-O3'	86.2(1)
[O1,O2',O3']/[O2,O3,O1'] twist 56.5			

octahedron. Structural features of the semiquinone ligands are in accord with their charge, including the pattern of ring C-C bond lengths.

As found for both $\text{Ga}(3,6\text{-DBSQ})_3$ and $\text{Al}(3,6\text{-DBSQ})_3$, $\text{Co}(3,6\text{-DBSQ})_3$ shows a broad NMR resonance in CDCl_3 solution at room temperature for the *tert*-butyl protons. At 17 °C this signal appears at 2.02 ppm (fwhm = 60 Hz), and it shifts and sharpens slightly to 2.08 ppm (fwhm = 45 Hz) at 35 °C. At temperatures where the NMR signal may be observed, the complex is EPR silent, but at lower temperatures in toluene solution, a simple first-derivative signal may be observed. In toluene glass at 77 K, the slightly anisotropic spectrum shown in Figure 7 is obtained. Organic radicals commonly show weakly anisotropic EPR spectra in solid matrices,¹³ and this signal is essentially the spectrum of a ligand-based radical. The spectrum is centered about a g value of 1.998, and weak ^{59}Co ($I = 7/2$) hyperfine coupling of 22.6 G appears on the low-field component of the signal.

The EPR spectrum of $\text{Co}(3,6\text{-DBSQ})_3$ is clearly different from spectra obtained on the Ga and Al analogs, and this apparent difference in magnetic ground state has been investigated using temperature-dependent magnetic measurements. A plot of magnetic moment vs temperature is shown in Figure 4 to contrast with the magnetic behavior of $\text{Ga}(3,6\text{-DBSQ})_3$. At 350 K, the magnetic moment of the cobalt complex is $3.04 \mu_B$, near the value expected for three noninteracting $S = 1/2$ centers, and as the plot shows, the magnetic moment drops with decreasing temperature to a value of $1.82 \mu_B$ at 5 K. This temperature dependence has been fit to the expression used to model the behavior of $\text{Ga}(3,6\text{-DBSQ})_3$, and the result appears as the solid line in the plot shown

Figure 7. EPR spectrum of $\text{Co}(3,6\text{-DBSQ})_3$ recorded in a toluene glass at 77 K.

in Figure 4.¹¹ Values of $J = -39.1 \text{ cm}^{-1}$, $g = 2.17$, and $\text{TIP} = 2.36 \times 10^{-4} \text{ emu/mol}$ were used to model temperature dependence, and the exchange interaction between radical ligands through the diamagnetic $\text{Co}(\text{III})$ ion is clearly antiferromagnetic. As a system consisting of three equivalent antiferromagnetically coupled $S = 1/2$ centers, spin frustration may be a factor contributing to magnetic behavior, but no evidence for this effect appears in either the magnetic behavior or the EPR spectrum. The difference in exchange between $\text{Ga}(3,6\text{-DBSQ})_3$ and $\text{Co}(3,6\text{-DBSQ})_3$ lies in the nature of metal π orbitals available to propagate coupling between semiquinone ligands (*vide infra*).

Zn(tmeda)(3,6-DBSQ)₂. The semiquinone complexes of Zn are among the earliest examples of compounds containing radical ligands coordinated with a diamagnetic metal ion. Neutral bis(quinone) complexes of zinc were reported by Bu'Lock and Harley-Mason in 1951 as products obtained by the oxidation of catechol and methylcatechol in the presence of Zn(II) and were formulated as containing radical semiquinone ligands on the basis of considerations of charge.¹⁴ The compounds were reported to be dark green and insoluble in organic solvents. Prokof'ev prepared $\text{Zn}(3,6\text{-DBSQ})_2$ by the reaction between zinc amalgam and 3,6-DBBQ,¹⁵ and McGarvey has prepared $\text{Zn}(3,5\text{-DBSQ})_2$ by a similar procedure.¹⁶ The presence of bulky *tert*-butyl substituents increases the solubility of these complexes in nonpolar solvents, enabling study of solution EPR spectra. Both diradical complexes show $\Delta M_S = 1$ and 2 signals with satellites associated with the perpendicular and parallel components of zero-field splitting arising from a coupled $S = 1$ spin state.

Attempts have been made to isolate both $\text{Zn}(3,6\text{-DBSQ})_2$ and $\text{Zn}(3,5\text{-DBSQ})_2$ in crystalline form for characterization of their structural and magnetic properties, but only amorphous solid samples have been obtained. When the synthesis of $\text{Zn}(3,6\text{-DBSQ})_2$ was carried out in the presence of an excess of tmeda, dark blue crystals of $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ were obtained. A view of the complex molecule is shown in Figure 8, and selected bond lengths and angles are listed in Table 7. The complex is octahedral in structure with average Zn-O and Zn-N bond lengths of 2.076(6) and 2.191(10) Å. Bond lengths of the semiquinone ligands are similar to features of other 3,6-DBSQ ligands with a C-O length of 1.27(1) Å and slightly contracted C-C lengths at the ring C3-C4 and C5-C6 positions. Ring carbon atoms of

(14) Bu'Lock, J. D.; Harley-Mason, J. *J. Chem. Soc.* 1951, 2248.(15) Prokof'ev, A. I.; Malysheva, N. A.; Bubnov, N. N.; Solodovnikov, S. P.; Kabachnik, M. I. *Dokl. Akad. Nauk SSSR* 1980, 252, 236.(16) Ozarowski, A.; McGarvey, B. R.; Peppe, C.; Tuck, D. G. *J. Am. Chem. Soc.* 1991, 113, 3288.(13) For example: Bresgunov, A. Y.; Dubinsky, A. A.; Poluektov, O. G.; Lebedev, Y. S.; Prokof'ev, A. I. *Mol. Phys.* 1992, 75, 1123.

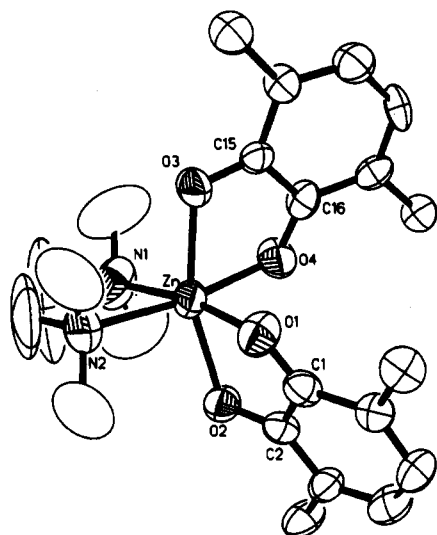


Figure 8. View of the $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ molecule.

Table 7. Bond Lengths and Angles for $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$

Bond Lengths (Å)			
Zn-O1	2.069(7)	Zn-O2	2.083(7)
Zn-O3	2.071(6)	Zn-O4	2.080(7)
Zn-N1	2.184(10)	Zn-N2	2.198(10)
O1-C1	1.251(13)	O2-C2	1.293(14)
C1-C2	1.487(14)	C2-C3	1.421(15)
C3-C4	1.359(18)	C4-C5	1.425(14)
C5-C6	1.357(15)	C1-C6	1.429(17)
O3-C15	1.280(10)	O4-C16	1.262(11)
C15-C16	1.475(13)	C16-C17	1.436(13)
C17-C18	1.360(13)	C18-C19	1.419(14)
C19-C20	1.344(12)	C15-C20	1.438(12)
Angles (deg)			
O1-Zn-O2	78.4(3)	O3-Zn-O4	78.2(2)
N1-Zn-N2	82.6(5)		

the ligand containing oxygen atoms O3 and O4 in the figure are bent out of the Zn, O3, O4 plane by 21° , due to a steric interaction between methyl groups bound to N1 and to *tert*-butyl carbon C25. Despite the large number of reports on semiquinones coordinated to Zn, this is the first such complex characterized structurally. As for $\text{Zn}(3,6\text{-DBSQ})_2$, the EPR spectrum of $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ (Figure 9) shows both $\Delta M_S = 1$ and 2 transitions. Satellites due to zero-field splitting with $D = 192 \times 10^{-4} \text{ cm}^{-1}$ appear for the $\Delta M_S = 1$ transition. This value compares with $177 \times 10^{-4} \text{ cm}^{-1}$ reported for $\text{Zn}(3,6\text{-DBSQ})_2$ ¹⁵ and $201 \times 10^{-4} \text{ cm}^{-1}$ observed for the product obtained by treating $\text{Zn}(3,5\text{-DBSQ})_2$ with tmeda.¹⁶ A sharp isotropic signal at $g = 2.003$ appears at the center of the $\Delta M_S = 1$ spectrum that has also been seen in the spectrum of $\text{Zn}(3,5\text{-DBSQ})_2$ and has been attributed to a low-level impurity.¹⁶

The electronic spectrum of $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ recorded in hexane solution consists of strong transitions at 212 nm ($69\,000 \text{ M}^{-1} \text{ cm}^{-1}$), and 306 (22 000) and a series of four transitions that are similar to those of $[3,6\text{-DBSQ}]^-$ shown in Figure 2. The two central bands appear at 719 nm (1020) and 817 (1050), with shoulders at 680 and 927 nm.

Magnetic measurements recorded on solid samples of $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ show a decreasing magnetic moment with decreasing temperature that is indicative of antiferromagnetic exchange between semiquinone radical ligands. Magnetic moment begins at a value of $2.42 \mu_B$ at 350 K, as shown in Figure 10, which is near the value of $2.45 \mu_B$ expected for two noninteracting $S = 1/2$ centers. At 5.9 K, the magnetic moment for the complex is $0.43 \mu_B$ and the temperature-dependent behavior has been fit to a Bleaney-Bowers expression for values of $J = -33.65 \text{ cm}^{-1}$ and $g = 1.95$.¹⁷ These measurements show that $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ has a spin-singlet ground state, and EPR



Figure 9. EPR spectrum of $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ recorded in a toluene glass at 77 K.

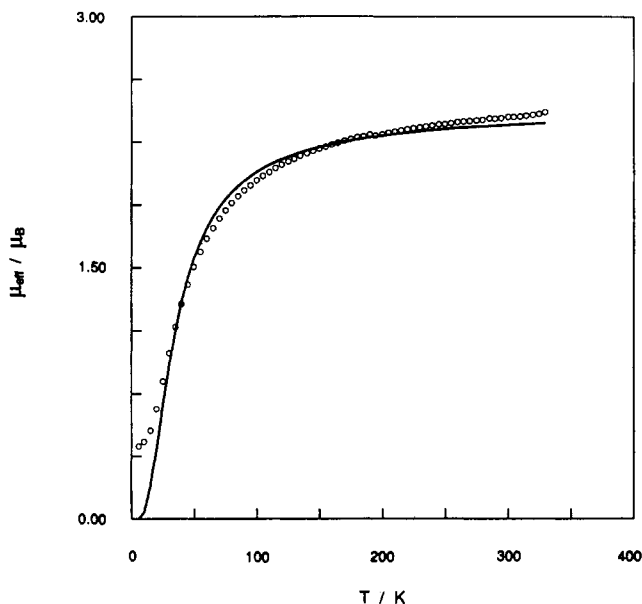


Figure 10. Plot of effective magnetic moment vs temperature for $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$. The solid line represents the theoretical fit for $J_{\text{SQ,SQ}} = -33.7 \text{ cm}^{-1}$.

activity must result from thermal population of the $S = 1$ excited state that lies 67.3 cm^{-1} above the diamagnetic ground state.

Ga(tmeda)(3,6-DBSQ)(3,6-DBCat). A persistent question that has been raised with the study of quinone complexes containing mixed-charge ligands concerns the extent to which interligand electron transfer occurs and the role that the central metal ion may play in mediating electron transfer. In conjunction with our studies on the magnetic properties of polyradical complexes of Ga, we have prepared $\text{Ga}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})$. Structurally, the complex molecule is similar to $\text{Co}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ and $\text{Fe}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})$.^{18,19} Both have been characterized crystallographically and have been found to have distinguishable, charge-localized semiquinone and catecholate ligands. The optical spectrum of $\text{Ga}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ closely resem-

(17) The temperature dependence of magnetic susceptibility was modeled using the Bleaney-Bowers equation for interacting $S = 1/2$ centers:

$$H = -2J_{\text{SQ,SQ}}S_1S_2$$

$$\chi_M = (2Ng^2\beta^2/kT)(3 + e^x)^{-1} + \text{TIP}$$

$$x = -2J_{\text{SQ,SQ}}/kT$$

The best theoretical fit for $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ was obtained with $J_{\text{SQ,SQ}} = -33.7 \text{ cm}^{-1}$, $g = 1.95$, and $\text{TIP} = 2.10 \times 10^{-4} \text{ emu/mol}$.

(18) Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.*, submitted for publication.
 (19) Attia, A.; Pierpont, C. G. *Inorg. Chem.*, submitted for publication.

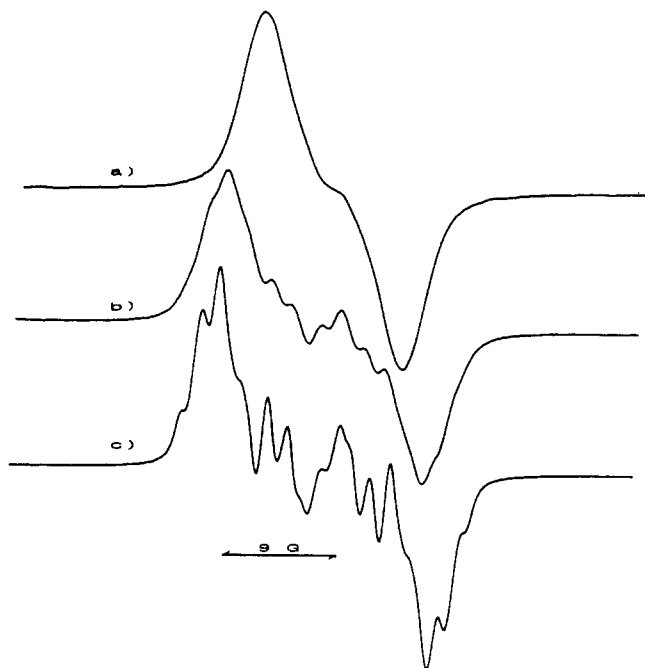


Figure 11. EPR spectra obtained for Ga(tmeda)(3,6-DBSQ)(3,6-DBCat) in toluene solution at temperatures of 335 K (a), 270 K (b), and 210 K (c).

bles the spectrum of Ga(3,6-DBSQ)₃, but with band intensities that are decreased by approximately a factor of two-thirds. Strong transitions appear at 221 nm (19 000 M⁻¹ cm⁻¹) and 297 (6500), a weaker band appears at 369 nm (850), and a broad transition with peaks at 805 nm (260) and 897 (270) appears in the visible–near-IR that resembles the structured low-energy band of the free [3,6-DBSQ]⁻ anion. The infrared spectrum of Ga(tmeda)(3,6-DBSQ)(3,6-DBCat) has a pattern of bands in the region between 1600 and 1000 cm⁻¹ that also appear in the spectra of Co(tmeda)(3,6-DBSQ)(3,6-DBCat) and Fe(tmeda)(3,6-DBSQ)(3,6-DBCat). It is therefore reasonable to assume that the gallium complex also has charge-localized semiquinone and catecholate ligands in the solid state.

EPR spectra have been recorded on Ga(tmeda)(3,6-DBSQ)(3,6-DBCat) in toluene solution at various temperatures with the result shown in Figure 11. At 335 K, the spectrum obtained is a simple first-derivative spectrum with no evidence of hyperfine coupling to the Ga nuclei or to ligand protons. As temperature is decreased, the spectrum broadens slightly and hyperfine lines due to both the semiquinone ring protons and the gallium nuclei appear with the most clearly resolved spectrum obtained at 210 K. The spectrum obtained at this temperature may be simulated with a coupling constant of 6.6 G to the $I = 3/2$ ⁶⁹Ga and ⁷¹Ga nuclei and 1.88 G to four equivalent semiquinone ring protons. The magnitude of the ring proton coupling is half the value normally observed for localized 3,6-DBSQ ligands,²⁰ and this, together with the equivalence of the ring protons on the two quinone ligands, shows that in solution at 210 K the unpaired electron is delocalized over both ligands on the EPR time scale. The loss of hyperfine resolution at higher temperatures appears associated with a dynamic process that will require further investigation to understand, but electron transfer between quinone ligands of different charges has been reported for complexes of Si, Sn, and P.²¹

Discussion

Metal-Mediated Magnetic Coupling between Semiquinone Radicals. Studies on magnetic exchange between radical semiquinone ligands and chelated paramagnetic metal ions have provided a simple model based on the relative orientation of magnetic axes.²² In situations where orbital symmetry is compatible, the interaction is antiferromagnetic; when metal and semiquinone π magnetic orbitals are orthogonal, the interaction is usually weakly ferromagnetic. Interradical coupling through a diamagnetic metal ion is more unusual. The series of ruthenium complexes, Ru^{II}L₂(SQ)₂ have been studied with a variety of semiquinones and coligands.²³ The complexes are all diamagnetic to the point of showing well-resolved NMR spectra. Strong antiferromagnetic exchange between radical ligands in these complexes is propagated by filled metal d_z orbitals that couple strongly with SQ_z levels. Similar interactions are responsible for the near-diamagnetism of members of the square planar M^{II}(SQ)₂ (M = Ni, Pd, Pt; SQ = 3,5-DBSQ, 3,6-DBSQ), series where filled out-of-plane metal and SQ_z orbitals couple.³ Further, the strength of interrational exchange increases down the series of metals with strongest coupling for Pt and the weakest for Ni. It is reasonable to expect that coupling between ligands of Co(3,6-DBSQ)₃ should be antiferromagnetic, as magnetic measurements confirm. Exchange is propagated through the filled Co(III) 3d_z level, and characterization of Ir(3,6-DBSQ)₃ has shown that the molecule has a single ligand-based unpaired electron at room temperature, further showing that interrational exchange increases down a congeneric group.²⁴ Stabilization of the filled d levels of the post transition elements apparently eliminates π -bonding contributions to interrational exchange. This is apparent from the magnetic similarity between Ga(3,6-DBSQ)₃ and its Al analog, where there is no filled d orbital. Weak coupling through orthogonal p orbitals results in weak ferromagnetic exchange in these cases with J values of 6.23 and 8.55 cm⁻¹ for Ga(3,6-DBSQ)₃ and Al(3,6-DBSQ)₃.

The complexes of Zn are of interest as cases where the 3d level is filled but apparently not stabilized to the point that coupling with a partially-filled ligand π level is eliminated. Indeed the interrational J values for Co(3,6-DBSQ)₃ and Zn(tmeda)(3,6-DBSQ)₂ are quite similar in magnitude and sign at -39.10 and -33.65 cm⁻¹, respectively. In this respect, Zn(II) clearly behaves as a transition metal ion.

Intramolecular Cat-SQ Electron Transfer. Complexes containing two quinone ligands that differ in charge are becoming common. Structural, spectroscopic, and magnetic properties sometimes provide clear insights on metal charge and often permit differentiation among BQ, SQ, and Cat forms of the ligands. Complexes of general form M^{III}(N-N)(SQ)(Cat) containing Co, Mn, and Fe are of this type.^{18,19,25} In other cases charge distribution is less clear, and a delocalized electronic structure may be an appropriate description. The Ru^{III}(N-N)(SQ)(Cat) complexes that may alternatively be described as Ru^{II}(N-N)(SQ)₂ species are perhaps of this type.²³ These compounds may be considered as a reversal of the ligand-bridged mixed-valence metal complexes where the extent to which metal ions are electronically coupled depends upon orbital interactions with the bridge. Coupling between SQ and Cat ligands in a complex molecule of general form ML₂(SQ)(Cat) will depend specifically upon π -bonding with the “bridging” metal ion. Hyperfine coupling resolved in the EPR spectra of complexes containing diamagnetic metals may be used to provide information on charge localization on the EPR time scale, and Prokof'ev has used this technique to

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study the dynamic exchange of charge between ligands of $P(3,5\text{-DBSQ})(3,5\text{-DBCat})_2$ and for the $[M(3,6\text{-DBSQ})(3,6\text{-DBCat})_2]^{2-}$ ($M = \text{Si, Sn}$) anions.²¹ Among transition metal compounds, the complexes best suited for such a study are the members of the $\text{Co}(\text{N-N})(\text{SQ})(\text{Cat})$ series.²⁵ However, at low temperature, only weak metal hyperfine structure is observed, and at higher temperatures, electron transfer to the metal, giving a high-spin, EPR-inactive, $\text{Co}(\text{II})$ species, $\text{Co}^{\text{II}}(\text{N-N})(\text{SQ})_2$, occurs. Coupling to the ring protons of one or both quinone ligands, if resolved, could provide information on charge localization on the EPR time scale.

Hyperfine coupling to the ring protons bonded at the ring 4- and 5-carbon atoms of 3,6-DBSQ is in the range 3.1–3.9 G for the coordinated semiquinone radical. Spin delocalization over two equivalent quinone ligands would decrease the magnitude of the hyperfine coupling by half.²¹ Significant delocalization into metal-based orbitals usually results in complete loss of SQ proton hyperfine coupling. The appearance of proton hyperfine coupling of 1.88 G to four equivalent ring protons in the EPR spectrum of $\text{Ga}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ in solution at 210 K implies that radical spin is distributed equally over both ligands. The absence of a concentration dependence for the observed spectral changes shown in Figure 11 points to an intramolecular mechanism for charge transfer between the two ligands. However, as the magnetic properties of $\text{Ga}(3,6\text{-DBSQ})_3$ show, there is no significant π -bonding with the metal and no viable electronic pathway through the metal bridge. The loss of all hyperfine resolution at higher temperatures in solution suggests a dynamic process. Whether this results from a tunneling mechanism for electron transfer or from rapid interligand transfer that occurs

intramolecularly within the solvent shell is not known and will require further investigation. The significant conclusion from this observation is that rapid electron transfer may occur between the two equivalent ligands, even for systems where electronic coupling between the ligands is weak.

A feature of mixed-valence transition metal complexes that may carry over to quinone complexes containing mixed-charge ligands is the intervalence-transfer (IT) transition. The appearance of these bands for mixed-valence metal complexes is an indication of the extent to which dissimilar metals interact through the bridge. The bands typically are of low energy, are broad, and show a predictable dependence upon solvent polarity. The optical spectrum of $\text{Ga}(\text{tmeda})(3,6\text{-DBSQ})(3,6\text{-DBCat})$ shows no evidence of an IT band, nor do the spectra of $\text{Fe}(\text{N-N})(\text{SQ})(\text{Cat})$ species. The $\text{Co}(\text{III})$ and $\text{Mn}(\text{III})$ complexes $\text{M}^{\text{III}}(\text{N-N})(\text{SQ})(\text{Cat})$ show transitions at low energy, in the 2000–3000-nm region, but these appear associated with $\text{Cat} \rightarrow \text{Co}(\text{III})$ or $\text{Mn}(\text{III}) \rightarrow \text{SQ}$ charge transfer.^{18,25} Bands often appear in the 1000-nm region for quinone complexes,²³ but these may be attributed to other types of bonding effects, and studies that may be used to identify low-energy transitions as IT bands have not been reported.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for $\text{Ga}(3,6\text{-DBSQ})_3$, $\text{Co}(3,6\text{-DBSQ})_3$, and $\text{Zn}(\text{tmeda})(3,6\text{-DBSQ})_2$ (31 pages). Ordering information is given on any current masthead page.