

# Metal(II) Derivatives of 3,5-Di-*tert*-butyl-1,2-*o*-benzoquinone. EPR Study of Conformation in Biradicals

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**Abstract:** The metals M = Mg, Zn, Cd, and Ba react with 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone to form the biradical compounds M(TBSQ)<sub>2</sub> (TBSQ = 3,4-di-*tert*-butyl-1,2-*o*-benzosemiquinone). In toluene, M(TBSQ)<sub>2</sub> reacts with neutral donor ligands (L = pyridine (py), 2,2'-bipyridine (bipy), and *N,N,N',N'*-tetramethylethylenediamine (tmed)) to produce 1:1 or 1:2 adducts. EPR spectra of M(TBSQ)<sub>2</sub> in toluene solutions show that these exist as oligomers instead of mononuclear species. Analysis of the EPR of mixtures of M(TBSQ)<sub>2</sub> (M = Mg, Zn, and Cd) and L (L = py, bipy, and tmed) in frozen solutions has demonstrated the existence of biradical species in which the interaction between two semiquinone ligands is purely dipolar in nature. For the monodentate ligand py both *cis* and *trans* isomers are identified, with the *cis* isomer by far the more abundant. Only the *cis* isomer is found for the bidentate ligands bipy and tmed. The tmed ligand produced additional species for M = Mg, Cd, and Ba, which are proposed as five-coordinate for M = Mg and eight coordinate for M = Cd and Ba.

## Introduction

Earlier, researchers in this laboratory reported a series of studies of the oxidative addition reactions of tin(II),<sup>1</sup> indium(I),<sup>2</sup> and indium(0)<sup>3</sup> with substituted *o*-benzoquinones to give the corresponding catecholato derivatives. EPR studies<sup>3-5</sup> of the reaction intermediates and products were critical in elucidating the reaction mechanism and the nature of the products. In one study,<sup>3</sup> we were able to react indium metal directly with 3,5-*tert*-butyl-1,2-*o*-benzoquinone (TBQ) to produce the semiquinone-indium(I) compound (TBSQ)In in solution, and this compound was isolated as a 1:1 adduct with 1,10-phenanthroline (phen) (TBSQ)In-phen.

In the present research, we have shown that a number of other metallic main group elements (M = Mg, Zn, Cd, Ba) will react directly with TBQ to give compounds of the form M(TBSQ)<sub>2</sub>, which further react with various ligands (L = pyridine (py), 2,2'-bipyridine (bipy), and *N,N,N',N'*-tetramethylethylenediamine (tmed)) to produce the adducts M(TBSQ)<sub>2</sub>*n*L. These compounds are biradicals with *S* = 1 and give appropriate EPR spectra. We have identified *S* = 1 spectra in frozen solutions that fit the spin Hamiltonian

$$\hat{H} = \beta B g \hat{S} + D[\hat{S}_z^2 - \frac{1}{3}S(S+1)] + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (1)$$

The spin-spin parameters *D* and *E* are determined by the dipole-dipole interaction between spins on the two semiquinone anions and, therefore, yield information on the conformation of the complexes in question.

It has been reported that the related quinone 3,6-*tert*-butyl-1,2-*o*-benzoquinone (DTBQ), which can be reduced to the semiquinone (DTBSQ) and catecholato (DTBC), will react with Zn,<sup>6,7</sup> Cd,<sup>6</sup> and Sn<sup>8</sup> amalgams to give the biradical compounds M(DTBSQ)<sub>2</sub>. Identification was based entirely on solution EPR spectra of reaction products and of species obtained by further reduction with sodium or potassium mirrors. No isolation of any products or other characterization was reported. For Sn<sup>7</sup> and Si,<sup>9</sup>

Table I. Analytical Results for M(TBTSQ)<sub>2</sub>*n*L Compounds

compound	M (%)		C (%)		H (%)	
	found	calcd	found	calcd	found	calcd
Zn(TBSQ) <sub>2</sub>	12.5	12.5	65.5	66.5	7.65	7.97
Zn(TBSQ) <sub>2</sub> ·2py	9.66	9.84	68.3	68.7	7.89	7.59
Zn(TBSQ) <sub>2</sub> ·bipy <sup>a</sup>	9.90	9.87				
Zn(TBSQ) <sub>2</sub> ·tmed	10.2	10.5				
Cd(TBSQ) <sub>2</sub>	20.3	20.3				
Cd(TBSQ) <sub>2</sub> ·2py	16.1	15.8				
Cd(TBSQ) <sub>2</sub> ·bipy	15.6	15.8				
Cd(TBSQ) <sub>2</sub> ·tmed	16.7	16.8				
Mg(TBSQ) <sub>2</sub>	5.08	5.23	71.6	72.3	8.49	8.67
Mg(TBSQ) <sub>2</sub> ·pt	4.50	4.47				
Mg(TBSQ) <sub>2</sub> ·bipy	4.00	3.91				
Mg(TBSQ) <sub>2</sub> ·tmed <sup>b</sup>	4.19	4.18	71.4	70.3	9.18	9.71
Ba(TBSQ) <sub>2</sub>			56.0	58.1	6.73	6.98

<sup>a</sup>N found (calcd): 4.44 (4.22). <sup>b</sup>N found (calcd): 4.47 (4.82).

the biradical species M(DTBSQ)<sub>2</sub>(DTBC) has been proposed to explain solution EPR results. The same reaction between tin amalgam and DTBQ has been reported<sup>8</sup> to produce Sn(DTBSQ)<sub>2</sub>(DTBQ), but again no isolation of the compound or independent characterization was done. Solution EPR results were also used<sup>10</sup> to identify the formation of compounds with *S* > 1 in the reaction of DTBQ with amalgams of Al, Ga, and In. In most of the studies with DTBQ (see above), EPR of frozen solutions were reported and values of *D* and *E* parameters obtained. In two instances,<sup>7,9</sup> attempts were made to calculate *D* and *E*, but these calculations are questionable because they assume the unpaired spin to reside entirely on the semiquinone oxygen atoms. In one study,<sup>7</sup> it is even suggested that the unpaired spin must be on only one of the semiquinone oxygen atoms.

## Experimental Section

**General Data.** Metals were cut in small pieces from zinc (mossy; Allied), cadmium (shot; Gallard Schlessinger), magnesium (turnings; Fisher) and barium (rod; Strem). Beryllium (powder; Strem), mercury (triple-distilled; Secmet), 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone (Aldrich), 2,2'-bipyridine (Aldrich), *N,N,N',N'*-tetramethylethylenediamine (Aldrich), and pyridine (Fisher) were used as supplied. Toluene and petroleum ether (35–60 °C) were dried over sodium and distilled before use. All operations were carried out in a dry nitrogen atmosphere.

Metal analyses were by atomic absorption spectrometry with an IL 251 instrument; microanalysis was by Guelph Chemical Laboratories Ltd. Infrared spectra in the 200–4000 cm<sup>-1</sup> region were recorded on the

(1) Annan, T. A.; Chadha, R. K.; Tuck, D. G.; Watson, K. *Can. J. Chem.* **1987**, *65*, 2670.

(2) Annan, T. A.; Tuck, D. G. *Can. J. Chem.* **1988**, *66*, 2935.

(3) Annan, T. A.; McConville, D. H.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *Inorg. Chem.* **1989**, *28*, 1644.

(4) Annan, T. A.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, 439.

(5) Annan, T. A.; Chadha, R. K.; Doan, P.; McConville, D. H.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *Inorg. Chem.* **1990**, *29*, 3936.

(6) Prokof'ev, A. I.; Malysheva, N. A.; Bubnov, N. N.; Solodovnikov, S. P.; Kabachnik, M. I. *Dokl. Chem. (Engl. Transl.)* **1980**, *2*, 236.

(7) Rakhimov, R. R.; Prokof'ev, A. I.; Lebedev, Y. S. *Khim. Fiz.* **1989**, *8*, 1265.

(8) Prokof'ev, A. I.; Prokof'ev, T. I.; Bubnov, N. N.; Solodovnikov, S. P.; Belostotskaya, I. S.; Ershov, V. V.; Kabachnik, M. I. *Dokl. Chem. (Engl. Transl.)* **1979**, *245*, 195.

(9) Prokof'ev, A. I.; Prokof'ev, T. I.; Bubnov, N. N.; Solodovnikov, S. P.; Belostotskaya, I. S.; Ershov, V. V.; Kabachnik, M. I. *Dokl. Chem. (Engl. Transl.)* **1977**, *234*, 276.

(10) Prokof'ev, A. I.; Bubnov, N. N.; Solodovnikov, S. P.; Kabachnik, M. I. *Dokl. Chem. (Engl. Transl.)* **1979**, *245*, 178.

Nicolet 5DX spectrometer with use of KBr pellets.

**Preparation of M(TBSQ)<sub>2</sub> Compounds.** The same general procedure was used throughout this paper. The metal (2.0–4.5 mmol) was weighed and placed in a 100-mL Schlenk flask containing a 2-fold excess of quinone, and toluene (30 mL) was then added via a syringe. The mixture was then refluxed at the boiling point of toluene for 24 h. With M = Cd and Mg, the M(TBSQ)<sub>2</sub> products partially precipitated during the reaction; at the end of the reflux, 50% of the solvent was removed under vacuum and the vessel kept at 0 °C for 24 h, after which the dark blue M(TBSQ)<sub>2</sub> compounds were collected by filtration and dried in vacuo. For M = Zn and Ba, the M(TBSQ)<sub>2</sub> produced by the above treatment is soluble, and the toluene was removed by pumping to dryness; the resulting solid was dried in vacuo. Solid Zn(TBSQ)<sub>2</sub> is dark blue in color, while Ba(TBSQ)<sub>2</sub> is dark green. The yields were essentially quantitative for Zn and Ba and better than 90% for Mg and Cd. Mercury and beryllium failed to react with the quinone under these conditions, and the metals were recovered at the end of prolonged refluxing (see Table I for analytical results).

**Preparation of M(TBSQ)<sub>2</sub>nL Compounds.** 1. **Pyridine (py) and N,N,N',N'-Tetramethylethanediamine (tmed) Adducts.** A weighed quantity of the M(TBSQ)<sub>2</sub> compound (M = Zn, Cd, Mg) (0.40–0.70 mmol) was treated with toluene (10 mL) and an excess of the liquid ligand (0.5 mL) added. The mixture was stirred for 30 min (M = Zn, Cd) or refluxed for 24 h (M = Mg). The solution was filtered (hot for Mg) and pumped to dryness to give the corresponding M(TBSQ)<sub>2</sub>nL compounds as dark blue solids in yields better than 90%. The reaction of Ba(TBSQ)<sub>2</sub> with py or tmed at room temperature produced solids having the following elemental analysis: pyridine reaction, C, 54.7, H, 6.43, N, 0.40; tmed reaction C, 54.6, H, 6.88, N, 1.99. These values suggest that the amount of ligand incorporated by the Ba(TBSQ)<sub>2</sub> compound is very low, particularly in the case of pyridine, but in any case no sensible formulation could be derived from these results.

2. **2,2'-Bipyridine (bipy) Adducts.** Equimolar amounts of M(TBSQ)<sub>2</sub> and bipy (0.40–0.70 mmol) were suspended in toluene (10 mL), and the solution was either stirred for 30 min (M = Zn, Cd) or refluxed for 24 h (M = Mg). The resulting solution was filtered (hot for Mg) and the solvent removed under vacuo to leave a dark green powder, which was washed with petroleum ether (2 × 2 mL) and dried in vacuo. The yields were better than 90%.

**Electron Paramagnetic Resonance Spectroscopy.** Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E12 instrument calibrated with an NMR gaussmeter. The klystron frequency was determined from the EPR spectrum of diphenylpicrylhydrazide. Low-temperature spectra were taken with use of a liquid nitrogen dewar insert in the cavity. Solutions were made with toluene and ligands in appropriate concentrations. In most instances, the concentration of M(TBSQ)<sub>2</sub> was of the order of 0.01 mol L<sup>-1</sup>. Liquid solution spectra were recorded with 5 mW of power and a modulation of 0.02 G. For frozen solution spectra, the power was 10–20 mW and the modulation was 1 G.

## Results

**I. Reaction of M with TBQ.** For M = Zn, Cd, Mg, and Ba, the analyses identify the formation of M(TBSQ)<sub>2</sub> in the reaction of metal with TBQ in refluxing toluene. The highly colored solids are all slightly soluble in toluene, py, and tmed. The presence of the TBSQ<sup>-</sup> anion in the products is evidenced by the EPR spectra, the color, and the infrared spectra. In free TBQ, important features of the IR spectrum are the very strong and broad band centered at 1654 cm<sup>-1</sup>, a medium-intensity band at 1567 cm<sup>-1</sup>, and a strong band at 1474 cm<sup>-1</sup>. The strong band at 1654 cm<sup>-1</sup>, identified as  $\nu(\text{C}=\text{O})$ , is completely absent in the product, confirming the reduction of the quinone.

**II. Reaction of M(TBSQ)<sub>2</sub> with Ligands.** The compounds M(TBSQ)<sub>2</sub> (M = Zn, Cd, and Mg) react in toluene to form 1:1 or 1:2 adducts M(TBSQ)<sub>2</sub>nL for the three ligands studied (L = py, bipy, and tmed). Ba(TBSQ)<sub>2</sub> does not appear to form stoichiometric derivatives with the same ligands under the conditions studied.

The IR spectra of these coordinated complexes have a band at 1583 ± 10 cm<sup>-1</sup>, which is identified as  $\nu(\text{C}=\text{C})$ , observed at 1567 cm<sup>-1</sup> in the free o-quinone. This shift is similar to that observed by Sofen et al.<sup>11</sup> in the spectra of similar chromium derivatives of TBSQ. The complexes also show a trio of strong absorptions centered at 1526 ± 10 cm<sup>-1</sup>, 1486 ± 6 cm<sup>-1</sup>, and 1456

± 10 cm<sup>-1</sup> similar to bands observed earlier<sup>3</sup> for related indium semiquinone derivatives. The correct assignment of these bands is difficult, since they possibly involve mixed vibrations such as  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{C})$  of the semiquinone ligand and vibrations of the nitrogen donor.

**III. EPR Spectra.** EPR spectra have been recorded for M(TBSQ)<sub>2</sub> (M = Zn, Cd, Mg, and Ba) as solid powders and in dilute solution in toluene at both room temperature and 77 K. Spectra have also been taken at the same temperatures of solutions to which various amounts of the ligands (py, bipy, and tmed) were added.

**A. EPR of M(TBSQ)<sub>2</sub>.** 1. **Liquid Solutions in Toluene.** In all cases, only one signal was observed, with a *g* value of ca. 2.003, typical of free radicals. No hyperfine splitting could be seen despite repeated attempts to dilute and deoxygenate the solutions. Peak to peak line widths were 5.2, 5.2, 29, and 23 G for Mg, Zn, Cd, and Ba, respectively.

2. **EPR of Frozen Toluene Solutions at 77 K.** Again only one resonance line was seen with the same *g* value observed at room temperature. Peak to peak line widths were 5, 8, 15, and 14 G for Mg, Zn, Cd, and Ba, respectively. A very weak half-resonant-field line, typical for *S* = 1 systems, was observed with an intensity 5000–10 000 times smaller than the main resonance. It will be argued later that this spectrum is primarily due to oligomeric and polymeric species.

3. **Solid Powders.** Spectra were similar to those observed in solutions but no half-resonant-field resonance was detected. The line widths, which are small for a solid, indicate that exchange narrowing is operating in the solid state.

**B. EPR of M(TBSQ)<sub>2</sub>nL in Solution.** 1. **Room Temperature Solutions.** The addition of excess ligand L (L = py, bipy, tmed) immediately produced a doublet spectrum with a splitting of 3.3 G in nearly every case, the exception being Ba(TBSQ)<sub>2</sub> with py or bipy. This is the typical spectrum of a TBSQ free radical anion bonded to a metal ion.<sup>3–5,12–15</sup> The splitting observed is due to the proton bonded to C4. No splitting from the proton bonded to C6 or from the *tert*-butyl groups could be resolved. In the cadmium compound, an additional splitting of 7.1 G was observed, from the <sup>111</sup>Cd and <sup>113</sup>Cd isotopes. The intensity of the doublet signal was more than 80% of the signal observed before addition of the ligand L.

The stoichiometry and the EPR results, discussed below, for the frozen solutions indicate that we are dealing with a biradical in which two semiquinone free radical anions are attached to M<sup>2+</sup>, with *S* = 1. Furthermore, the intensity of the Cd hyperfine in the room temperature solution indicates that there is little or no dissociation to give free TBSQ<sup>-</sup> ions. If there were any appreciable coupling between the two spins in M(TBSQ)<sub>2</sub>, we would expect a triplet pattern in the EPR spectrum instead of the doublet pattern observed, so that two TBSQ<sup>-</sup> radicals in M(TBSQ)<sub>2</sub> are behaving in solution as independent *S* = 1/2 systems, with negligible exchange interaction between the ligands. The only coupling between the two spins is, therefore, dipolar in nature, and this is averaged out by the tumbling motions in the room temperature solutions. The small exchange interaction between the two semiquinone radicals is supported by the size of the Cd hyperfine interaction, which indicates a spin density of 0.15% in the Cd *s* orbital (the Fermi contact term of -13.65 GHz was assumed<sup>16</sup> for Cd).

This lack of exchange coupling between  $\pi$  electrons in ligands attached to the same metal ion is surprising and needs further study. It may not be the first system found in which this occurs, however. EPR, NMR, optical, and electrochemical studies<sup>17–22</sup>

(12) Eaton, D. R. *Inorg. Chem.* **1964**, *3*, 1268.

(13) Ryba, O.; Pilar, J.; Petránek, J. *J. Coll. Czech. Chem. Commun.* **1986**, *33*, 26.

(14) Lucken, E. A. C. *J. Chem. Soc.* **1964**, 4234.

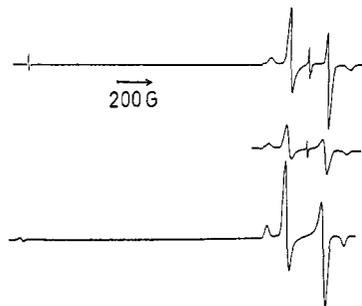
(15) Felix, C. C.; Sealy, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 1555.

(16) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

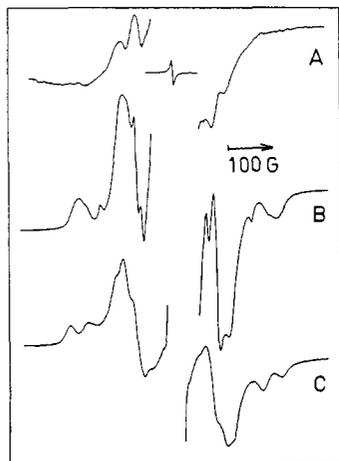
(17) Motten, A. G.; Hanck, K.; DeArmond, M. K. *Chem. Phys. Lett.* **1981**, *79*, 541.

(18) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 3032.

(11) Sofen, S. R.; Ware, D. C.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 234.



**Figure 1.** EPR spectrum of  $\text{Zn}(\text{TBSQ})_2$ -tmed dissolved with excess tmed in toluene at 77 K is the top spectrum. The bottom spectrum is a computer simulation of the biradical portion of the spectrum, and the center spectrum is a simulation including 1.5% of an isotropic signal.



**Figure 2.** EPR spectra at 77 K for  $\text{Mg}(\text{TBSQ})_2$  in toluene and pyridine for various py:Mg ratios: (A) 10:1; (B) 100:1; and (C) 500:1.

of the species  $\text{M}(\text{bipy})_3^{1-}$ ,  $\text{M}(\text{bipy})_3^0$ , and  $\text{M}(\text{bipy})_3^{1+}$  ( $\text{M} = \text{Fe}(\text{II})$ ,  $\text{Ru}(\text{II})$ , and  $\text{Os}(\text{II})$ ) have been interpreted in terms of a model in which each unpaired electron resides in one ligand  $\pi$  orbital with no exchange interaction with the other ligand  $\pi$  electrons. No ligand hyperfine interactions were resolved in the liquid EPR spectra of these systems, however.

**2. Frozen Solutions at 77 K.** Well-resolved  $S = 1$  spin-triplet spectra were observed in frozen solutions. In every case, the spectra contained a sharp line at  $g = 2.003$  similar in width to that observed in frozen solutions of  $\text{M}(\text{TBSQ})_2$  in the absence of the ligand L. The intensity of this central peak decreased with increasing concentration of L but never disappeared completely. It appears prominent only due to its small width compared to the 400-G widths of the spin-triplet spectra, and simulations of the spectra show that this center line has an intensity of no more than a few percent of the total observed intensity. The centers of the triplet spectra are shifted upfield by 4 G with respect to the central resonance. A half-resonant-field transition was observed, 5–10 times less intense than the main triplet spectrum. It was centered 7 G below the half-resonant field. A good example of this spin-triplet spectrum is shown in Figure 1. In this case, the central peak was very low in intensity and the half-field transition is quite prominent.

**L = py.** The spectra for both the Mg and Zn salts changed with concentration of py. Figure 2 shows the EPR spectra of  $\text{Mg}(\text{TBSQ})_2$  for several values of the py:Mg mole ratio, and Figure 3 shows the same for  $\text{Zn}(\text{TBSQ})_2$ . In the case of  $\text{Mg}(\text{TBSQ})_2$ ,

**Table II.** Zero-Field Parameters for  $\text{M}(\text{TBSQ})_2\text{-npy}$

M	(py:M)	intensity	$D$ ( $10^{-4} \text{ cm}^{-1}$ )	$E$ ( $10^{-4} \text{ cm}^{-1}$ )
Mg	<100	broad complex signal		
	>100	strong	$202 \pm 5$	<8
		weak	$159 \pm 2$	$5 \pm 2$
		pure py	$215 \pm 2$	
Zn	0.5	strong	$200 \pm 2$	
		weak	$222 \pm 5$	
		strong	$199 \pm 2$	
		weak	$176 \pm 5$	
	20	80%	$159 \pm 2$	
		20%	$197 \pm 2$	<7
Cd	pure py		$163 \pm 2$	<7
	>1.5	30%	$197 \pm 2$	<7
		70%	$165 \pm 2$	<5
	pure py		$147 \pm 2$	<5
Ba		no triplet signal observed		

**Table III.** Zero-Field Parameters for  $\text{M}(\text{TBSQ})_2\text{-nbipy}$

M	intensity	$D$ ( $10^{-4} \text{ cm}^{-1}$ )	$E$ ( $10^{-4} \text{ cm}^{-1}$ )
Mg		$193 \pm 5$	<7
Zn	weak	$236 \pm 2$	<6
	strong	$202 \pm 2$	<6
Cd		$156 \pm 2$	$18 \pm 2$
Ba		no triplet signal observed	

**Table IV.** Zero-Field Parameters for  $\text{M}(\text{TBSQ})_2\text{-ntmed}$

M	intensity	$D$ ( $10^{-4} \text{ cm}^{-1}$ )	$E$ ( $10^{-10} \text{ cm}^{-1}$ )
Mg	70%	$216 \pm 5$	<8
	30%	$180 \pm 5$	<8
Zn		$201 \pm 5$	<7
Cd	weak	$169 \pm 2$	
	strong	$100 \pm 10$	
Ba		$196 \pm 2$	<3

a broad complex signal is observed for py:Mg ratios below 100, but for ratios considerably greater than 100 two distinct triplet signals are identified. For  $\text{Zn}(\text{TBSQ})_2$ , four triplet signals could be identified for py:Zn ratios as low as 0.5, and as this ratio increased two of these signals diminished greatly in intensity, leaving two prominent signals. In pure pyridine solution, only one triplet signal is observed. For  $\text{Cd}(\text{TBSQ})_2$ , two triplet signals start appearing when py:Cd > 1.5 and no other signals appear or disappear with increasing concentration. In pure pyridine, only the more intense signal is detected. No triplet signal is detected for  $\text{Ba}(\text{TBSQ})_2$  at any pyridine concentration.

**L = bipy.** Spectra for  $\text{M}(\text{TBSQ})_2\text{-n}(\text{bipy})$  at high bipy:M ratios are shown for  $\text{M} = \text{Mg}$ ,  $\text{Zn}$ , and  $\text{Cd}$  in Figure 4.  $\text{Mg}(\text{TBSQ})_2$  behaves with bipy much as it does with pyridine in that, at low bipy:Mg ratios, we observed a broad complex spectrum, which gradually decreased in intensity with increasing bipy concentration and was replaced by a single triplet resonance. This triplet spectrum is identified at ratios as low as 10 and becomes the dominant resonance when bipy:Mg > 50. At very high ratios (1000), a weak second triplet resonance is detected. For  $\text{Zn}(\text{TBSQ})_2$ , two triplet resonances are detected for bipy:Zn ratios as low as 1:8. As the ratio is increased, the resonance with the larger splitting becomes weaker but never disappears completely. In the case of  $\text{Cd}(\text{TBSQ})_2$ , a single triplet resonance appears at bipy:Cd = 0.25 and improves in quality with increasing concentration of bipy. No triplet resonance is detected for  $\text{Ba}(\text{TBSQ})_2$  at any bipy concentrations studied.

**L = tmed.**  $\text{Zn}(\text{TBSQ})_2$  gives a single triplet resonance at all concentrations at which it is seen (tmed:Zn > 1), whereas  $\text{Mg}(\text{TBSQ})_2$  and  $\text{Cd}(\text{TBSQ})_2$  each display two triplet resonances.  $\text{Ba}(\text{TBSQ})_2$  gives a single triplet resonance but only about 70 h after the solution is prepared. During this interval, the intensity of the central peak decreases by a factor of 15, as shown in Figure 5.

(19) Angel, S. M.; DeArmond, M. K.; Donohoe, R. J.; Hanck, K. W.; Wertz, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 3688.

(20) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem.* **1983**, *149*, 115.

(21) Ohsawa, Y.; DeArmond, M. K.; Hanck, K. W.; Morland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383.

(22) Morris, D. E.; Hanck, K. W.; DeArmond, M. K. *Inorg. Chem.* **1985**, *24*, 977.

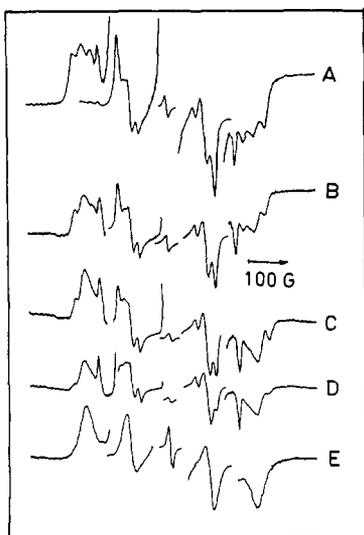


Figure 3. EPR spectra at 77 K for Zn(TBSQ)<sub>2</sub> in toluene and pyridine for various py:Zn ratios: (A) 1:2; (B) 1:1; (C) 2:1; (D) 3:1; and (E) pure py as solvent.

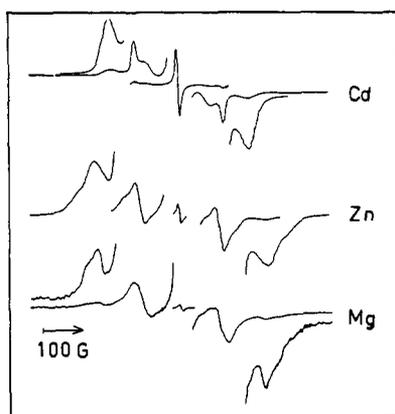


Figure 4. EPR spectra at 77 K for M(TBSQ)<sub>2</sub> in toluene and excess bipy. Increase in gain in the wings is  $\times 100$  and  $\times 1000$  relative to the central portion of the spectrum.

**Analysis of Triplet Spectrum. I. Zero-Field Splitting Parameters.** The triplet spectra were interpreted in terms of the spin Hamiltonian of (1). In the analysis of the frozen solution spectra, we assumed the  $g$  matrix to be isotropic. The values of  $D$  and  $E$  were found from the spectra with Wasserman's formulas.<sup>23</sup> In some cases, the spectra were simulated with our own computer programs based on an analytical calculation of the resonant fields in randomly oriented spin triplet systems,<sup>24</sup> and such a simulation is shown in Figure 1. In general, however, it was found sufficient to measure the field differences between the outside maxima and minima and between the center pair of peaks to obtain  $D$  and  $E$  values. These features were reasonably well resolved, even in overlapping spectra. The values of  $D$  and  $E$  given in Tables II–IV are absolute values since we cannot determine the sign.

Since the values of  $D$  and  $E$  depend mainly on molecular geometry, it is of interest to discover if we can use these results to determine the conformations of the observed biradicals, and we have therefore attempted to calculate  $D$  and  $E$  from the dipolar model.

**II. Calculations of Zero-Field Parameters.** The zero-field splitting in the systems studied here is the result of dipole–dipole interactions between the two unpaired electrons. Since there is no evidence of any exchange interaction, the model assumes that

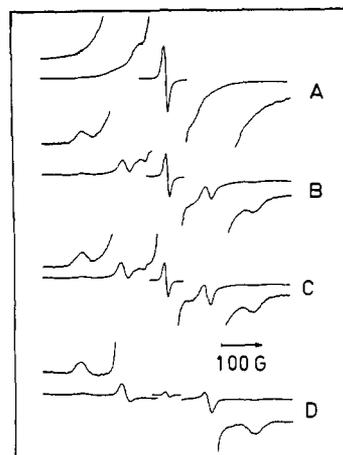


Figure 5. EPR spectra at 77 K for Ba(TBSQ)<sub>2</sub> plus excess tmed in toluene for different periods of time after mixing: (A) fresh solution; (B) 3 h; (C) 5 h; and (D) 70 h.

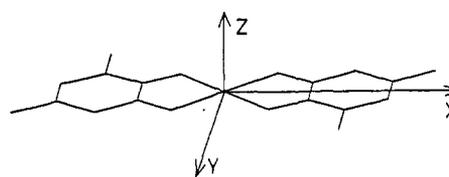


Figure 6. System of coordinates used in calculations of  $D$  and  $E$ .

each electron is delocalized over only one semiquinone ligand. We further assume a point dipole model in which the spin is distributed among the eight  $p$  orbitals of the six carbon and two oxygen atoms of the semiquinone. The  $p$  orbital is approximated by dividing the spin density into two centers, 0.7 Å above and below the ring.<sup>25–27</sup> The components of the  $D$  matrix are then calculated by summing the point dipole interaction of all 16 centers in one ligand with the 16 centers on the other. The equation is<sup>25–29</sup>

$$D_{mn} = \frac{g^2 \beta^2}{2} \sum_{i=1}^{16} \sum_{j=1}^{16} \rho_i \rho_j [\delta_{nm} - 3\gamma_n \gamma_m] r_{ij}^{-3} \quad (2)$$

where  $\rho_i$  is the fraction of spin density at site  $i$ , and  $\gamma_n$  is the direction cosine for the  $r_{ij}$  vector to the  $n$  coordinate axis. The  $D$  matrix is then diagonalized by applying the Jacobi method to obtain  $D_{xx}$ ,  $D_{yy}$ , and  $D_{zz}$ . The parameters  $D$  and  $E$  for the spin Hamiltonian can then be calculated from the equations

$$D = \frac{1}{2}(2D_{zz} - D_{xx} - D_{yy}) \quad E = \frac{1}{2}(D_{xx} - D_{yy}) \quad (3)$$

In the calculation, the values of  $r_{ij}$  and  $\gamma_n$  were obtained by assuming a symmetrical ligand system in which the lengths of 1.44 and 1.28 Å<sup>30</sup> were assumed for the C–C and C–O bonds, respectively. The O–C–C angles were assumed to be 120°, and the M–O bond lengths were taken to be the sum of ionic radii. The validity of this assumption is justified by comparing the  $r(\text{M–O})$  distances in Table V for Zn and Cd with (averaged) bond lengths of 2.11 and 2.235 Å, respectively, found in complexes with M–(O<sub>2</sub>)<sub>2</sub>N<sub>2</sub> kernels.<sup>31</sup> The O–M–O bite angle was then calculated to fit the rest of the structure. In the calculation of  $D$  and  $E$  for various configurations, the trans isomer (Figure 6) was chosen initially. Other configurations were then generated by rotating one semiquinone ring consecutively about the  $x$ ,  $y$ , and  $z$  axes by the angles  $\alpha$ ,  $\beta$ , and  $\gamma$ . The idealized cis configuration, for example, would have  $\alpha = 90^\circ$ ,  $\beta = \gamma = \pm 45^\circ$ .

To estimate the spin density parameters ( $\rho_i$ ), we resorted to simple Hückel theory as outlined in various texts<sup>32,33</sup> and varied

(23) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

(24) Baranowski, J.; Cukierda, T.; Jezowska-Trzebiatowska, B.; Kozlowski, H. *Chem. Phys. Lett.* **1976**, *39*, 606.

(25) Mukai, K.; Sogabe, A. *J. Chem. Phys.* **1980**, *72* (1), 598.

(26) Higuchi, J. *J. Chem. Phys.* **1963**, *38*, 1237.

(27) Pullman, A.; Kochanski, E. *Int. J. Quantum Chem.* **1967**, *1*, 251.

(28) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press: Oxford, England, 1970.

(29) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173.

(30) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(31) Annan, T. A.; Peppe, C.; Tuck, D. G. *Can. J. Chem.* **1990**, *68*, 423.

**Table V.** Calculated Zero-Field Parameters for  $M(\text{TBSQ})_2\text{L}_2$ 

M	M-O (Å)	$\alpha$	$\beta$	$\gamma$	configuration	$D$ ( $10^{-4}$ cm $^{-1}$ )	$E$ ( $10^{-4}$ cm $^{-1}$ )
Mg	1.98	90	0	0	pseudotetrahedral	-149	0
		0	0	0	trans	-160	-4
		180	0	0		-160	-4
		90	45	45	cis	-227	-10
		270	45	45		-236	-11
Ba	2.66	90	0	0	pseudotetrahedral	-70	0
		0	0	0	trans	-71	-1
		180	0	0		-71	-1
		90	45	45	cis	-107	-1
		270	45	45		-110	-2
Zn	2.06	90	0	0	pseudotetrahedral	-134	0
		0	0	0	trans	-142	-4
		180	0	0		-142	-4
		90	45	45	cis	-206	-7
		270	45	45		-213	-8
Cd	2.29	90	0	0	pseudotetrahedral	-102	0
		0	0	0	trans	-105	-2
		180	0	0		-105	-2
		90	45	45	cis	-157	-4
		270	45	45		-162	-4

the parameters to fit known hyperfine splittings obtained from EPR spectra. In simple Hückel theory, the Coulomb integrals for oxygens and the C-O resonance integrals are approximated by the expressions<sup>32,33</sup>

$$\alpha(\text{X}) = \alpha(\text{C}) + h(\text{X})\beta(\text{CC}) \quad \beta(\text{XY}) = k(\text{XY})\beta(\text{CC}) \quad (4)$$

Felix and Sealy<sup>15</sup> have determined the spin density distribution in free and complexed benzosemiquinone radicals. We find that setting  $h(\text{X}) = 1.5$  and  $k(\text{XY}) = 0.9$  reproduces satisfactorily their result for the free radical and increasing  $h(\text{X})$  to 1.55–1.60 reproduces the metal complex spin densities. For *tert*-butylsemiquinone, we have taken  $h(\text{X}) = 1.55$  and simulated the replacement of hydrogen atoms by *tert*-butyl groups at C3 and C5 by altering the Coulomb integrals at those sites. In doing this, we attempted to reduce the spin density at C6 to give a value of 0.3 G or less for the hydrogen splitting.<sup>30</sup> In unsubstituted benzosemiquinone, the density predicts  $A_{\text{H}}(6) = 0.6$  G. In an earlier study,<sup>5</sup> we obtained a resolution of the  $\text{In}(\text{TBSQ})(\text{py})_2\text{Cl}_2$  spectrum, which showed hyperfine splittings of 0.3 G for the *tert*-butylhydrogens at the C5 but no evidence of any  $A_{\text{H}}(6)$  splitting. This condition could be met by reducing the C3 and C5 Coulomb integrals by 0.1  $\beta(\text{CC})$  with respect to those of the other carbon atoms. We find that small changes of this type in  $\rho_i$  have little effect on the calculated values of  $D$  and  $E$ . The electron spin densities used in the calculations were O1, 0.166; C2, 0.211; C3, 0.034; C4, 0.117; C5, 0.136; C6 0.012; C7, 0.182; and O8, 0.142.

Table V gives the calculated values of cis and trans forms of  $M(\text{TBSQ})_2\text{L}_2$ . We have also included the pseudotetrahedral configuration that might be expected as the most probable configuration for  $M(\text{TBSQ})_2$ . There is little difference between the trans and pseudotetrahedral configurations. The magnitude of  $D$  for the cis configuration is considerably larger as might be expected since the rings are closer together in this form.

## Discussion

**$M(\text{TBSQ})_2$  Systems.** The EPR spectra of  $M(\text{TBSQ})_2$  compounds in both liquid and frozen toluene solutions are almost the same as that in the powder, and this is only consistent with the presence of oligomeric species in the solution. In other words, we are detecting a powder spectrum in liquid and frozen solutions. There is good spectroscopic evidence that complexes of Mg, Ca, Sr, and Ba with bidentate keto enolate ligands  $\text{OC}(\text{R})\text{CHC}(\text{R}')\text{O}^-$  ( $\text{R} = \text{R}' = \text{CH}_3$ , *t*- $\text{C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_5$ ;  $\text{R} = \text{CH}_3$ ,  $\text{R}' = \text{C}_6\text{H}_5$ ) may be monomeric, oligomeric, or polymeric depending on R, the phase, and or solvent.<sup>34</sup> Given the low dielectric constant and noncom-

plexing nature of toluene, highly polar species such as  $M(\text{TBSQ})_2$  almost certainly exist in oligomeric form in solution, through intermolecular oxygen bridging.

**$M(\text{TBSQ})_2$  Adducts.** The formation of adducts of  $\text{ML}_2$  compounds with neutral mono- and bidentate donors such as py, bipy, and tmed is authenticated for each of the metals studied in the present research.<sup>34,35</sup> The reported coordination numbers for such complexes vary between six and nine, although eight- and nine-coordination is only observed for the large  $\text{Ba}^{2+}$  ion. The formation of complexes involving bipy (or 1,10-phenanthroline) or tmed (or ethylenediamine) with magnesium  $\beta$ -diketonates with zero, one, or two  $\text{CF}_3$  groups depends on both the properties of the neutral ligand and the extent of trifluoromethylation.<sup>36</sup> We may therefore expect a range of coordination numbers in solutions containing complexes with  $M(\text{TBSQ})_2$  and py, bipy, or tmed. An additional and important factor is that, while  $M(\text{TBSQ})_2\text{L}_2$  complexes where L = monodentate ligand may be in either cis or trans pseudooctahedral stereochemistry, those with a bidentate neutral ligand should only give a cis isomer. The asymmetry of the  $\text{TBSQ}^-$  ligand means that further differentiation is possible, in principle, between syn and anti orientations of these two ligands. Calculations (see below and Table V) show that the  $D$  values for the two cis species could differ enough to be detected, and our experimental results do indeed indicate the existence of two forms of the cis isomer in some cases. In principle, the trans isomer can also have two forms, but the values of  $D$  (Table V) differ by less than  $10^{-4}$  cm $^{-1}$  for the two forms, and therefore their detection is unlikely considering the experimental conditions encountered in this research.

The reported values of  $D$  for  $\text{Zn}(\text{DTBSQ})_2$ <sup>7</sup> and  $\text{Cd}(\text{DTBSQ})_2$ <sup>6</sup> in THF are similar to the values we found for the corresponding TBSQ compounds in py and to the calculated values for the cis form of the complex. For  $\text{Si}(\text{DTBSQ})_2(\text{DTBC})$  in frozen toluene solution, the values of  $D = |301 \times 10^{-4}$  cm $^{-1}|$  and  $E = |22 \times 10^{-4}$  cm $^{-1}|$  were found<sup>9</sup> and our calculations for this compound give  $D = 316 \times 10^{-4}$  cm $^{-1}$  and  $E = -25 \times 10^{-4}$  cm $^{-1}$ , in excellent agreement.

Two resonances were found by Rakhimov et al.<sup>7</sup> for what they assumed to be  $\text{Sn}(\text{IV})(\text{DTBSQ})_2(\text{DTBC})$  with  $D$  values of  $|151 \times 10^{-4}$  cm $^{-1}|$  and  $|108 \times 10^{-4}$  cm $^{-1}|$  with  $E = 0$ , and the existence of two species was explained by assuming that the unpaired spin resided on only one oxygen atom in the ligand. For this compound, we would expect only one species with  $D = -210 \times 10^{-4}$  cm $^{-1}$ , but

(34) Fenton, D. E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 3, Chapter 23, p 27.

(35) Prince, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 5, Chapter 56, p 1.

(36) Fenton, D. E. *J. Chem. Soc. A* 1971, 3481.

(32) Levine, I. N. *Quantum Chemistry*, 2nd ed.; Allyn and Bacon: Boston, 1974; Chapter 15.8.

(33) Streitwieser, A. Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; Chapter 5.

it is interesting to note that we calculate  $D = -162 \times 10^{-4} \text{ cm}^{-1}$  and  $-109 \times 10^{-4} \text{ cm}^{-1}$  for the cis and trans forms of Sn(II). It should be noted that an earlier paper<sup>8</sup> suggested the same reaction used by Rakhimov et al. produced Sn(II) compounds instead of a Sn(IV) compound. Further research on reactions between elemental Sn and *o*-quinones would appear to be needed.

We will discuss our EPR results for the individual metals.

**Mg(TBSQ)<sub>2</sub>.** This compound behaves differently from the corresponding Zn and Cd species in that, for both py and bipy, the triplet spectra typical for Mg(TBSQ)<sub>2</sub>L<sub>2</sub> become visible only at large L:M ratios (50–100), whereas they are readily detected at ratios less than 1 in the case of Zn or Cd. It should be noted that, in the M(TBSQ)<sub>2</sub>·*n*(py) compounds isolated, *n* = 1 for M = Mg and *n* = 2 for M = Zn and Cd, in keeping with the tendency of Mg to form five-coordinate species.<sup>34</sup> At lower L:Mg ratios, a complex resonance was detected with splittings smaller than those found for the cis and trans isomers, and we suggest that this spectrum comes from some type of oligomeric species with *S* > 1. We have attempted preliminary calculations for such systems that show that their spectra would be complex and have smaller splittings than those of the simpler biradicals. Apparently, the small Mg<sup>2+</sup> radius makes such small clusters more stable than a monomeric complex at low concentrations of amines.

For L = py and high L:py ratios, two resonances were detected with *D* values close to those calculated for the cis and trans isomers. The trans resonance had a very low intensity relative to the cis resonance and disappeared when pure pyridine was used for the solvent. *D* for the cis resonance is smaller than calculated, but only small changes from the ideal cis structure are required to give the experimental value. When pyridine was used as the solvent, two cis resonances were detected, with the main resonance having a *D* value closer to the calculated value. For L = bipy, only the cis resonance was detected. At very high concentrations of bipy (bipy:Mg > 100), a second cis resonance became visible.

Two resonances were found for L = tmed, with the main peak having a *D* value close to that calculated for the cis isomer. The other peak had a *D* value ( $180 \times 10^{-4} \text{ cm}^{-1}$ ) intermediate between cis and trans values. One explanation for this would be a five-coordinate complex in which tmed is acting as a monodentate ligand.

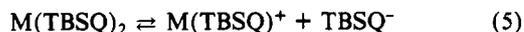
**Zn(TBSQ)<sub>2</sub>.** For L = py at high py:Zn ratios, we find two resonances that can be assigned as cis and trans, with the cis resonance of greater intensity. As with Mg(TBSQ)<sub>2</sub>, the trans resonance is absent when the solvent is pyridine. At very low py:Zn ratios, two other resonances are seen, and these diminish in intensity as the py concentration is increased. The resonance with  $D = 176 \times 10^{-4} \text{ cm}^{-1}$  is probably that of a five-coordinate complex. The species with  $D = 222 \times 10^{-4} \text{ cm}^{-1}$  could be the second cis isomer. 2,2'-Bipyridine also gives a weak resonance with  $D = 236 \times 10^{-4} \text{ cm}^{-1}$  as well as the main resonance with  $D = 202 \times 10^{-4} \text{ cm}^{-1}$ , but only one cis resonance is seen with L = tmed.

**Cd(TBSQ)<sub>2</sub>.** For L = py, two resonances are seen but both have *D* values close to that calculated for the cis isomers. Only the more intense cis resonance is detected when pyridine is the solvent. For L = bipy, only one cis resonance is seen. When L = tmed, a weak resonance is seen with a *D* value consistent with that for a cis isomer. The more intense resonance has  $D = 100 \times 10^{-4} \text{ cm}^{-1}$ , which is what we calculate for a trans isomer. The only reasonable explanation for this signal would be to assume that the larger size of the Cd<sup>2+</sup> ion allows for eight-coordination with two tmed ligands coordinated and the TBSQ<sup>-</sup> ions in a trans orientation. As will be seen below, eight-coordination is also required to explain the tmed-Ba(TMSQ)<sub>2</sub> results.

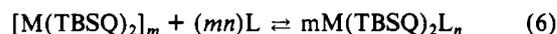
**Ba(TBSQ)<sub>2</sub>.** Ba<sup>2+</sup> has the largest ionic radius of all the metals studied and should therefore form the weakest complexes. Of the

ligands studied, only tmed is able to break down the clusters of Ba(TBSQ)<sub>2</sub> to produce simple biradicals with one barium atom, and this is a very slow reaction. The *D* value observed, however, is much larger in magnitude than can be accounted for in a hexacoordinate complex. We observe that the magnitude of *D* can be roughly related to the angle between the vectors connecting the metal atom to the center of each TBSQ<sup>-</sup> ring. For trans isomers, this angle is 180°, and for cis isomers it is 120°. The *D* value observed requires this angle to be 90°. This could occur for 8-fold coordination if we had a squashed cube or antiprism with a cis conformation for the two TBSQ<sup>-</sup> ligands.

**M(TBSQ)<sub>2</sub> Equilibria.** The dissociation of M(TBSQ)<sub>2</sub> in solution can be described by the conventional equation



and comparison with acac complexes<sup>37</sup> of Mg, Zn, Cd, and Ba suggests that the equilibrium constant (i.e., the reciprocal of the stability constant (*K*<sub>2</sub>)) is of the order of 10<sup>-3</sup>. We find no evidence for the existence of any measurable concentration of TBSQ<sup>-</sup> in the solutions studied, presumably because association of M(TBSQ)<sub>2</sub> into oligomers (see above) reduces the concentration of M(TBSQ)<sub>2</sub> to low levels. In the presence of neutral donors, the spectroscopic evidence is that the solution contains mononuclear species M(TBSQ)<sub>2</sub>L<sub>*n*</sub>, and we are dealing with the equilibrium



This equilibrium lies strongly to the right for M = Cd and Zn. For M = Mg and L = py or bipy, the equilibrium constant is smaller (100-fold excess of L required) and intermediate species involving more than one magnesium atom are indicated. The equilibrium lies to the left for M = Ba and L = py or bipy. It lies to the right for L = tmed, but the rate of equilibration is very slow.

## Conclusions

The direct reaction of metals with 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone has proved to be an effective method of preparing biradical complexes M(TBSQ)<sub>2</sub> (M = Mg, Zn, Cd, and Ba). In toluene solution, these compounds react readily with nitrogen-donor ligands (py, bipy, and tmed) to produce the adducts M(TBSQ)<sub>2</sub>·*n*L. The EPR of toluene solutions of M(TBSQ)<sub>2</sub> suggests that the solute is some sort of cluster that breaks up into molecular units M(TBSQ)<sub>2</sub>·*n*L when neutral ligands are added to the solution.

Analysis of the EPR of mixtures of M(TBSQ)<sub>2</sub> (M = Mg, Zn, Cd) and L (L = py, bipy, tmed) in frozen toluene solutions has demonstrated the existence of biradical species in which the interaction between the two semiquinone rings is purely dipolar in nature. The analysis has shown that, for the monodentate ligand py, both cis and trans isomers exist, but the cis isomer is by far the most abundant, and in pure pyridine it is the only form found. As expected, only the cis form is found with the bidentate ligands bipy and tmed. The tmed ligand produced additional species for M = Mg, Cd, and Ba, and these are proposed to be five-coordinate species for M = Mg and eight-coordinate species for M = Cd and Ba.

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(37) Stary, J.; Liljenzin, J. O. *Pure Appl. Chem.* 1982, 54, 2557.