Supplementary Material Available: A textual presentation of the details of the SCF–Xα–SW calculations, ORTEP diagrams, and tables of bond distances, bond angles, and general displacement parameters (14 pages); listings of structure factors (31 pages). Ordering information is given on any current masthead page.

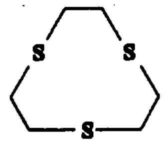
Contribution from the Departments of Chemistry,
University of Tennessee at Chattanooga,
Chattanooga, Tennessee 37403,
and University of Alabama in Huntsville,
Huntsville, Alabama 35899

Benzene Trisulfide, the Strongest Field Thioether Ligand: Its Nickel(II) Complex[1]

Gregory J. Grant,*[2a] Carolyn D. Grant,[2a,b]
and William N. Setzer[2c]

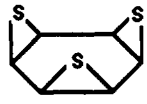
Received July 12, 1990

During the past few years there has been a period of intense activity in the complexation of transition-metal ions with mesocyclic (small ring) and macrocyclic thioether ligands, and several excellent review articles dealing with the coordination chemistry of these ligand systems have recently appeared.[3-6] Most of the work on crown thioether ligands has centered on the nine-membered-ring trithioether 1,4,7-trithiacyclononane (9S3). This important ligand has currently been complexed to over 25 transition-metal ions and p-block metal ions with the majority of this research appearing during the past 5 years.



structure of 9S3

A critical aspect relating to the unique complexation properties of 9S3 is its preferred [333] conformation in which all of the sulfur atoms are endodentate.[7-9] Because of this conformation, the ligand does not have to undergo any conformational changes in order to coordinate to a metal ion in a bis octahedral fashion. The importance of the preferred conformation of thioether ligands with regards to their coordination characteristics has been highlighted by other workers and by us.[5,10-12] We have been interested in how structural and conformational alterations of thioether ligands affect their complexation properties, and we have recently reported a complexation study of several ten-membered trithioethers as well as the synthesis of eleven-membered and twelve-membered ring trithioether ligands.[10,11] In order to continue to explore the relationship between organic structure and coordination characteristics, we wish to report the preparation of the bis nickel(II) complex of the highly rigid crown trithioether benzene trisulfide, BTS (*cis*-2,5,8-trithiatetracyclo$[6.1.0.0^{4,6}.0^{7,9}]$nonane).



structure of BTS

Note that benzene trisulfide, like 9S3, can function as a tridentate ligand. The sulfur atoms in the BTS molecule are rigidly locked in a endodenate conformation. Benzene trisulfide is an example of a heterohomoaromatic system.[13] These interesting ligand systems (including the analogous amine and crown ether heterohomoaromatic systems) were first prepared by Prinzbach and co-workers during the 1970s.[14,15] Wieghardt and Chaudhuri have noted that because of difficulties in the synthesis of these ligands, the coordination behavior of these ligands has not been examined.[16] To our knowledge only two other transition-metal complexes containing heterohomoaromatic ligand systems have appeared in the literature.[17,18]

We selected nickel(II) as the first transition-metal ion to be complexed with BTS for several reasons. The d–d absorption spectra of octahedral Ni(II) complexes are readily interpretable in terms of ligand field parameters, and a plethora of electronic spectroscopic data exists for nickel(II) complexes. The syntheses and spectral data for several hexakis(thioether)nickel(II) complexes have already appeared in the literature, and structural information currently exists on five of these complexes.[5,7,10,19,20] Finally, Ni(II) has historically been important in examining the properties of complexes involving macrocyclic and mesocyclic thioether ligands in the pioneering works of Black and McLean with 18S6 (1,4,7,10,13,16-hexathiacyclooctadecane), Busch and Rosen with 12S3 (1,5,9-trithiacyclododecane), and Setzer and co-workers with 9S3.[7,21-23]

Experimental Section

Materials. All materials were used as received except nitromethane, which was dried by standard methods.[24]

Measurements. Chemical analyses were performed by Galbraith Laboratories, Knoxville, TN. Solution spectra were measured by using

---

(1) Synthesis and Complexation Studies of Mesocyclic and Macrocyclic Polythioethers. 7. Part 6: Setzer, W. N.; Guo, Q.; Grant, G. J. *Heteroat. Chem.* **1990**, *1*, 425. This work was presented in part at the 39th Southeastern Regional Meeting of the American Chemical Society; Orlando, FL, Nov 3–6, 1987.

(2) (a) University of Tennessee at Chattanooga. (b) Undergraduate Research Scholar, University of Tennessee at Chattanooga. (c) University of Alabama in Huntsville.

(3) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

(4) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141.

(5) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1.

(6) Schroder, M. *Pure Appl. Chem.* **1988**, *60*, 517.

(7) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.

(8) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068.

(9) Discussion of the [333] nomenclature: Dale, J. *Acta Chem. Scand.* **1973**, *27*, 1115.

(10) Setzer, W. N.; Cacioppo, E. L.; Guo, Q.; Grant, G. J.; Kim, D. D.; Hubbard, J. L.; VanDerveer, D. V. *Inorg. Chem.* **1990**, *29*, 2672-2681.

(11) Setzer, W. N.; Afshar, S.; Burns, N. L.; Ferrante, L. A.; Hester, A. M.; Meehan, E. J., Jr.; Grant, G. J.; Isaac, S. M.; Laudeman, C. P.; Lewis, C. M. *Heteroat. Chem.* **1990**, *1*, 375.

(12) Wolf, R. E., Jr.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.

(13) Prinzbach, H.; Kagabu, S. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 252.

(14) Schwesinger, R.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 989.

(15) Schwesinger, R.; Fritz, H.; Prinzbach, H. *Chem. Ber.* **1979**, *112*, 3318.

(16) Chaudhuri, P.; Wieghardt, K. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons, Inc.: New York, 1987; p 336.

(17) Schwesinger, R.; Piontek, K.; Littke, W.; Schweikert, O.; Prinzbach, H.; Kruger, C.; Tsay, Y.-H. *Tetrahedron Lett.* **1982**, *23*, 2427.

(18) Prinzbach and co-workers have reported the synthesis of the perchlorate salt of $[Ni(BTS)_2]^{2+}$ and its characterization via elemental analysis and mass spectrometry: Kagabu, S.; Kaiser, C.; Keller, R.; Becker, P. G.; Muller, K.-H.; Knothe, L.; Rihs, G.; Prinzbach, H. *Chem. Ber.* **1988**, *121*, 741.

(19) Cooper, S. R.; Rawle, S. C.; Hartman, J. R.; Hintsa, E. J.; Admans, G. A. *Inorg. Chem.* **1988**, *27*, 1209.

(20) Wieghardt, K.; Kuppers, H.-J.; Weiss, J. *Inorg. Chem.* **1984**, *24*, 3067.

(21) Black, D. St. C.; McLean, I. A. *Aust. J. Chem.* **1969**, *22*, 3961.

(22) Black, D. St. C.; McLean, I. A. *Aust. J. Chem.* **1971**, *24*, 1401.

(23) Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262.

(24) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1970; p 120.

0020-1669/91/1330-0353$02.50/0 © 1991 American Chemical Society

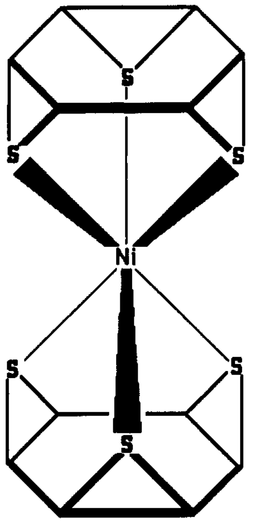
a Hitachi 100-80 ultraviolet–visible spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1310 infrared spectrophotometer.

Preparation of BTS. The ligand BTS was prepared from *cis*-benzene trioxide by the method of Prinzbach and Kagabu, and the compound was characterized by its NMR and UV spectra.[13] We would like to note one minor modification in the procedure for the synthesis of the intermediate isothiouronium salt. Under the high humidity conditions in our laboratory the salt proved to be extremely hygroscopic, necessitating its isolation under a nitrogen atmosphere.

Preparation of $[Ni(BTS)_2](BF_4)_2$. The complex was prepared by the method of Rosen and Busch.[23] A sample containing 25.0 mg (0.143 mmol) of BTS was dissolved in 5 mL of THF. A 0.0350 M stock solution of Ni(II) was prepared by using a mass of 119 mg (0.350 mmol) of nickel tetrafluoroborate hexahydrate, $Ni(BF_4)_2 \cdot 6H_2O$, 214 mg (2.10 mmol, 0.198 mL) of acetic anhydride, and a sufficient volume of nitromethane to bring the final volume of the stock solution to 10.00 mL. A 2.00-mL aliquot of the nickel(II) stock solution was removed and added, with stirring, to the BTS solution. The color of the reaction solution gradually changed from green to reddish brown following addition of the nickel solution, and a red-brown solid had formed after several minutes of stirring. The solid was filtered out and washed with two 10-mL portions of anhydrous ether to yield 14.5 g (39.2%) of bis(benzene trisulfide)-nickel(II) tetrafluoroborate. The complex, like the ligand itself, is very unstable and decomposes within hours in the solid state. It must be stored away from light, heat (temperatures <−78 °C), and oxygen. IR (KBr, cm^{-1}): 2989, 2950, 1470, 1340, 1160–1030 (s, BF_4^-), 920, 858, 802, 739, 623. The electronic spectrum measured in nitromethane shows two absorbances with λ_{max}'s at 768 nm (ϵ = 31) and 518 nm (ϵ = 33). The equivalent conductivity in nitromethane measured with a 0.0010 M solution is 175 Ω^{-1} cm^2 mol^{-1} (2:1 electrolyte). Anal. Calcd for $C_{12}H_{12}S_6NiB_2F_8$: C, 24.82; H, 2.08; S, 33.13. Found: C, 25.00, H, 2.09; S, 33.24.

Results

The electronic absorption spectrum, IR spectrum, conductivity measurements, and elemental analysis are all consistent with the proposed structure, which is shown as follows:



proposed structure of $[Ni(BTS)_2]^{2+}$

Each BTS ligand functions as a facially coordinating tridentate ligand. The absorption spectra of the complex are typical for hexakis(thioether) complexes of nickel(II).[5,10] The infrared spectrum indicates that complexation of the BTS has not caused the ligand to open into its π heterohomoaromatic form but remains in the σ form, as had been previously illustrated.[13] We hoped that complexation would stabilize this ligand; however, the complex readily decomposes, presumably to a nickel(II) sulfide species.

Table I. Ligand Field Parameters for Hexakis(thioether)nickel(II) Complexes

complex	*Dq*, cm^{-1}	f^b	β^c	ref
$[Ni(BTS)_2]^{2+}$	1302	1.50	0.66	this work
$[Ni(9S3)_2]^{2+}$	1271	1.46	0.64	7, 20
$[Ni(10S3)_2]^{2+}$	1239	1.42	0.63	10
$[Ni(keto\text{-}10S3)_2]^{2+}$	1201	1.38	0.73	10
$[Ni(ttn)_2]^{2+}$	1134	1.30	0.79	*d*, 19
$[Ni(12S3)_2]^{2+}$	1120	1.29	0.75	23, 5
$[Ni(24S6)]^{2+}$	1105	1.27	0.66	19
$[Ni(18S6)]^{2+}$	1227	1.41	0.83	19
$[Ni(tme)]^{2+}$	1225	1.41	0.63	19
$[Ni(dth)_3]^{2+}$	1110	1.28	0.76	25

[a] Ligand abbreviations: ttn = 2,5,8-trithianonane; 9S3 = 1,4,7-trithiacyclononane; 10S3 = 1,4,7-trithiacyclodecane; keto-10S3 = 1,4,7-trithiacyclodecan-9-one; 12S3 = 1,5,9-trithiacyclododecane; 18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane; 24S6 = 1,5,9,13,17,21-hexathiacyclotetracosane; tme = 1,1,1-tris((2-(methylthio)ethyl)thio)-ethane; dth = 2,5-dithiahexane. [b] Jorgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer: New York, 1969; pp 84–85. [c] Ratio of *B*(complex)/*B*(free ion), where *B*(free ion) for Ni(II) = 1041 cm^{-1}. [d] Unpublished results from our laboratories.

An octahedral complex of Ni(II) would be expected to exhibit three spin-allowed d–d transitions corresponding to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. However, the last of these transitions is usually obscured in thioether complexes due to an intense sulfur–metal charge-transfer band. We observe the two low-energy d–d transitions in the BTS complex. Ligand field parameters have been calculated for the nickel(II) complexes, and these are shown in Table I. Since the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is obscured, the value of *B*, the interelectronic repulsion parameter, is calculated by using the following equation:

$$B = \frac{2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2}{15\nu_2 - 27\nu_1}$$

Note that the large field strength of the BTS ligand (1302 cm^{-1}) is the largest of any thioether ligand and among the largest of any known neutral ligand. A listing of the ligand field parameters for over 40 octahedral Ni(II) complexes in a recent monograph shows no *Dq* values as large as the one that we have obtained for the BTS complex.[25] We attribute this large value to the rigid endodentate conformation of the BTS ligand causing the field strength of the BTS complex to be larger even than that of the 9S3 complex. The ordering of the ligand field strengths for the various thioether ligands in Table I underscores the importance of the preferred conformation of the ligand and the effects that these conformational constraints have on the complexation properties of the ligand.

The value of the Racah parameters, *B*, for the BTS complex is calculated to be 689 cm^{-1}. The nephelauxetic ratio (β = *B*(complex)/*B*(free ion)) for Ni(II)–thioether complexes is usually approximately 0.7, and the value of the BTS complex falls in this range.[18] In contrast, this ratio in amine complexes of Ni(II) is around 0.9.[18] A high degree of covalency between metal and thioether ligand orbitals is indicated by this relatively low value.

It is important to note that the 9S3 ligand adopts an endodentate conformation whereas weaker field crown thioether ligands such as 12S3 adopt an exodentate conformation.[5,10] The BTS is rigidly locked into its endodentate conformation, and these conformational effects manifest themselves in the unusual spectroscopic properties of its Ni(II) complex. The BTS complex is an additional example of how conformational factors exert critical effects on the complexation characteristics of the thioether ligands. Molecular models indicate that the area of a triangle formed by three facially coordinating sulfur atoms of a BTS molecule would occupy 73% less area than a similar triangle of sulfur atoms in 9S3.

There is a strong correlation in thioether complexes between ligand field strength and bond distance.[5,10] Because a strong field thioether ligand typically has short metal–sulfur bonds, we predict that the nickel–sulfur bond distances in the BTS complex will be compressed as well. We would like to note that the Co–N bonds in the bis Co(III) complex of the heterohomoaromatic amine benzenetriimine are extremely short (average Co–N bond distance 1.912 Å).

Conclusions

Benzene trisulfide generates the largest ligand field of any

---

[25] Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; p 508.

thioether ligand due to its rigid endodentate conformation. Our result highlights the important relationship between the preferred conformation of thioether ligands and their coordination behavior.

Acknowledgment. We thank Professor Doctor Horst Prinzbach of the University of Freiburg for his generous gift of *cis*-benzene trioxide and for his invaluable assistance in the preparation of BTS.

Contribution from the Department of Chemistry
and the Center for Organometallic Research,
University of North Texas, Denton, Texas 76203-5068,
and the Institute for Inorganic Chemistry, University of
Witten/Herdecke, 5810 Witten, FRG

Chelate Ring Closure in (*o*-Phenanthroline)$M(CO)_5$ Transients (M = Cr, Mo, W) Generated by Pulsed Laser Flash Photolysis

Shulin Zhang,[1a] Volker Zang,[1b] Gerard R. Dobson,*[1a] and Rudi van Eldik*[1b]

Received July 10, 1990

Chelate ring closure in $(\eta^1\text{-bid})M(CO)_5$ complexes (bid = bidentate, potentially chelating ligand; M = Cr, Mo, W; eq 1)

$$(\eta^1\text{-bid})M(CO)_5 \rightarrow (\eta^2\text{-bid})M(CO)_4 + CO \quad (1)$$

has been studied both for systems in which $(\eta^1\text{-bid})M(CO)_5$ can be isolated[2] and for systems where such species can be produced in situ and have sufficient lifetimes (>s) that they can be probed via diode array UV–visible[3,4] or rapid-scan FTIR[5] spectrophotometry. More recently, where the presence of rigid bidentate ligands afford yet more reactive (bid)$M(CO)_5$ species in which bid is formally monodentate, they have been produced via pulsed laser flash photolysis and studied on the microsecond to millisecond time scales. Thus, Oishi[6] and Kalyanasundaram[7] have investigated chelate ring closure in (phen)$M(CO)_5$ (phen = *o*-phenanthroline), while Zhang and Dobson have studied this process for conversion of (NBD)$Mo(CO)_5$ to (NBD)$Mo(CO)_4$ (NBD = norbornadiene).[8] In the studies of Oishi[6] and Zhang and Dobson,[8] evidence was presented that supports significant interaction between the noncoordinated functional group of the rigid bidentate ligand and the $M(CO)_5$ moiety prior to extrusion of CO through chelate ring closure.

The present investigation further probes possible interactions of this type in (phen)$M(CO)_5$ produced in situ after pulsed laser flash photolysis through determination of thermal activation parameters and volumes of activation accompanying chelate ring closure (eq 1); these data provide related but complementary information about the ring-closure process. The previously unreported rates of chelate ring closure in (phen)$Cr(CO)_5$ have also been obtained.

Experimental Section

Materials. $Cr(CO)_6$ and $W(CO)_6$ (Pressure Chemical Co.) and $Mo(CO)_6$ (Climax Molybdenum Co.) were vacuum-sublimed before use. Fluorobenzene (Aldrich Chemical Co.) was fractionally distilled from P_4O_{10} under nitrogen. *o*-Phenanthroline (Aldrich) was used as obtained.

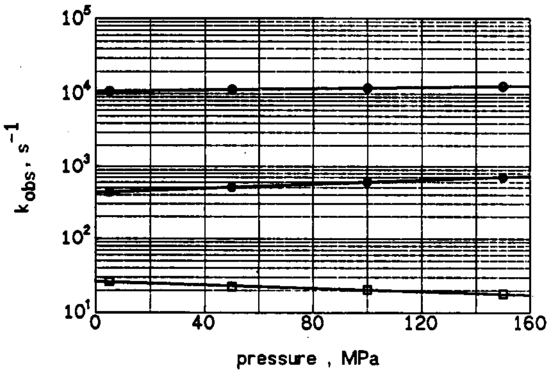


Figure 1. Plots of log k_{obsd} vs pressure for ring-closure reactions taking place after pulsed laser flash photolysis of $M(CO)_6$/fluorobenzene/*o*-phenanthroline (=0.05 M) solutions at 25.00 (5) °C. Top to bottom: M = Mo, W, Cr.

Kinetics Studies. The pulsed laser flash photolysis studies were carried out by employing a Lumonics TE-430 excimer laser ($Xe/F_2/He$ gas mixture at 351 nm, 25-mJ maximum energy, and 14-ns fwhi per pulse). Other details of the flash photolysis apparatus have been given elsewhere.[9] For studies at ambient pressure, a jacketted quartz cuvette was employed. The equipment for the variable-pressure studies (to 150 MPa), which employed a quartz "pillbox" observation cell,[10] also has been described previously.[11,12] Since it has been shown that benzene, the solvent employed in the previous studies,[6,7] freezes at ambient temperature at pressures >80 MPa,[13] fluorobenzene (FB) was employed as the solvent in this investigation. The kinetics and mechanism of the reaction steps (eq 2) that generate (L)$M(CO)_5$ after flash photolysis of M-

$$M(CO)_6 \xrightarrow{h\nu} [M(CO)_5] \xrightarrow{+FB} (FB)M(CO)_5 \xrightarrow{+L} LM(CO)_5 + FB \quad (2)$$

$(CO)_6$/L/FB solutions have been studied in detail for several L (=1-hexene, piperidine, pyridine) both at ambient pressure[14] and at variable pressures to 150 MPa.[15] Consequently, these steps, through which (phen)$M(CO)_5$ species are generated in situ on the microsecond time scale, are not further discussed here.

Solutions ca. 3×10^{-3} M in $M(CO)_6$ containing large excesses (>0.05 M) of phen were employed so that pseudo-first-order reaction conditions obtained. The monitoring wavelengths for formation of (phen)$M(CO)_4$ from (phen)$M(CO)_5$ according to eq 1 were 500–520 nm, as reported previously.[6,7] Values of the pseudo-first-order rate constants, k_{obsd}, were determined from data of 1–10 kinetics traces, depending on the observed signal-to-noise ratio. Data were analyzed by employing Asyst-based computer programs developed in-house. The limits of error, given in parentheses as the uncertainties of the last digit(s) of the experimental values, are one standard deviation.

Results and Discussion

Plots of ln $(A_\infty - A_t)$ vs time (A_∞ and A_t are the absorbances at infinite time and time *t*, respectively) at various temperatures are linear, consistent with pseudo-first-order kinetics behavior. The changes in absorbance are attributable to the formation of (phen)$M(CO)_4$ from (phen)$M(CO)_5$ via chelate ring closure.[6,7] Values of the pseudo-first-order rate constants, k_{obsd}, were obtained from the slopes of these plots. Data for four or five concentrations over a 2.5–5-fold concentration range, depending upon M, demonstrated that the rates for chelate ring closure are independent of [phen]. Thus the data obey the rate law

$$-d[(phen)M(CO)_5]/dt = k[(phen)M(CO)_5] \quad (3)$$

where *k* are first-order rate constants for chelate ring closure. The rate data are in reasonable agreement with those of the previous studies,[6,7] despite use of fluorobenzene rather than benzene as

---

(1) (a) University of North Texas. (b) University of Witten/Herdecke.

(2) (a) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 347. (b) Connor, J. A.; Hudson, G. A. *J. Organomet. Chem.* **1974**, *73*, 351. (c) Connor, J. A.; Riley, P. I. *J. Organomet. Chem.* **1975**, *94*, 55. (d) Connor, J. A.; Hudson, G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1025.

(3) (a) Schadt, M. J.; Lees, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 506. (b) Schadt, M. J.; Lees, A. J. *Inorg. Chem.* **1985**, *24*, 2942. (c) Chan, L.; Lees, A. J. *Inorg. Chim. Acta* **1986**, *113*, L3.

(4) Schadt, M. J.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 672.

(5) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 5784.

(6) Oishi, S. *Organometallics* **1988**, *7*, 1237.

(7) Kalyanasundaram, K. *J. Phys. Chem.* **1988**, *92*, 2219.

(8) Zhang, S.; Dobson, G. R. *Inorg. Chem.* **1990**, *29*, 598.

(9) Zhang, S.; Dobson, G. R. *Inorg. Chem.* **1989**, *28*, 324.

(10) le Noble, W. J.; Schlott, R. *Rev. Sci. Instrum.* **1976**, *47*, 770.

(11) Awad, H. H.; Dobson, G. R.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1839.

(12) Spitzer, M.; Gaertig, F.; van Eldik, R. *Rev. Sci. Instrum.* **1988**, *59*, 2092.

(13) Zhang, S.; Dobson, G. R. *Inorg. Chem.* **1990**, *29*, 3477.

(14) Zhang, S.; Dobson, G. R. *Polyhedron*, in press.

(15) Zhang, S.; Zang, V.; Bajaj, H. C.; Dobson, G. R.; van Eldik, R., *J. Organomet. Chem.*, in press.

0020-1669/91/1330-0355$02.50/0