Contribution from the Departments of Inorganic Chemistry and Magnetism, Indian Association for the Cultivation of Science, Calcutta 700032, India, and Department of Physics, Jadavpur University, Calcutta 700032, India

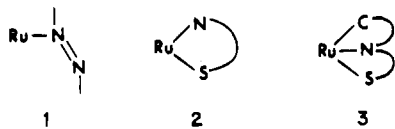# Ruthenium Complexes of N,S- and C,N,S-Coordinating Azo Ligands: Synthesis, Reactions, and Structure

Amiya K. Mahapatra,[1a] Sachchidananda Datta,[1a] Sreebrata Goswami,[1a] Monika Mukherjee,[1b] Alok Kumar Mukherjee,[1c] and Animesh Chakravorty*[1a]

The reaction of ruthenium trichloride with 2-(arylazo)phenyl thioethers (ArNNC$_6$H$_4$SR: Ar = Ph, *p*-tolyl; R = Me, CH$_2$Ph) (HL, **4**) in methanol affords blue-violet Ru(HL)(L)Cl (**8**) and red-violet RuL$_2$ (**6**), the former being the major product. If lithium bromide is added to the reaction mixture, the bromo analogue of **8** is formed. Both **8** and **6** contain pseudooctahedral ruthenium(II): HL is bidentate, coordinating via thioether sulfur and an azo nitrogen, but L is meridionally tridentate (coordination at sulfur, nitrogen, and the ortho carbon of Ar). All chelate rings are five-membered. The dissimilar binding of HL and L is reflected in infrared and ^{1}H NMR data. Considerable lowering of $\nu_{N=N}$ occurs in going from HL to **6** and **8** due to Ru–azo π-back-bonding. The conversion **8** → **6** is very effectively catalyzed (yield of **6** 60%) by a mildly hot (323 K) silica gel surface. The same conversion can be achieved but in poorer yield by reaction with silver perchlorate in methanol solution. A mechanism is suggested involving ortho-metalative edge displacement assisted by electrophilic (silver(I), silica gel) halide displacement. With two HL-like moieties bridged as in ArNNC$_6$H$_4$S(CH$_2$)$_3$SC$_6$H$_4$NNAr (Ar = Ph, *p*-tolyl, *m*-tolyl; H$_2$LL, **9**), octahedral hexadenticity of the type RuC$_2$N$_2$S$_2$ is readily achieved in violet Ru(LL) (**10**). The ortho metalation of the Ar groups (i.e. absence of two ortho protons) in **10** is unequivocally revealed by the spin–spin structure of the ^{1}H NMR spectrum of **10**. All three types of complexes (**6**, **8**, and **10**) exhibit reversible or nearly reversible ruthenium(III)/ruthenium(II) couples in cyclic voltammetry (platinum electrode, MeCN solvent). The formal potentials are as follows: RuL$_2$$^+$/RuL$_2$, ~0.52 V; Ru(LL)$^+$/Ru(LL), ~0.60 V; Ru(HL)(L)-Cl$^+$/Ru(HL)(L)Cl, ~0.70 V. The oxidized complexes are relatively unstable and have not been isolated in the pure state. However the electronic structure of coulometrically produced Ru(HL)(L)Cl$^+$ and RuL$_2$$^+$ in solution could be studied with the help of EPR and near-IR spectra. In frozen dichloromethane (77 K) the EPR spectrum of Ru(HL)(L)Cl$^+$ is rhombic (g_x = 2.291, g_y = 2.173, and g_z = 1.963 in the case Ar = Ph and R = CH$_2$Ph) and corresponds to axial (Δ) and rhombic (*V*) splitting parameters of 10 200 and 4700 cm^{-1} respectively. On the other hand the spectrum of the corresponding RuL$_2$$^+$ complex is axial ($g_\perp$ = 2.213 and $g_\parallel$ = 1.965), with Δ = 9800 cm^{-1}. The predicted near-IR absorptions due to transitions within Kramers doublets are experimentally observable. The ruthenium(II) complexes **6**, **8**, and **10** show multifeatured absorptions in the region 450–750 nm believed to be due to MLCT excitations. The axial splittings here (estimated to be <4000 cm^{-1}) are much less than those in the oxidized complexes.

Introduction

This work stems from our interest[2–5] in the chemistry of ruthenium coordinated to azo ligands. A persistent feature of the azo–ruthenium(II) chromophore (**1**) is the presence of substantial
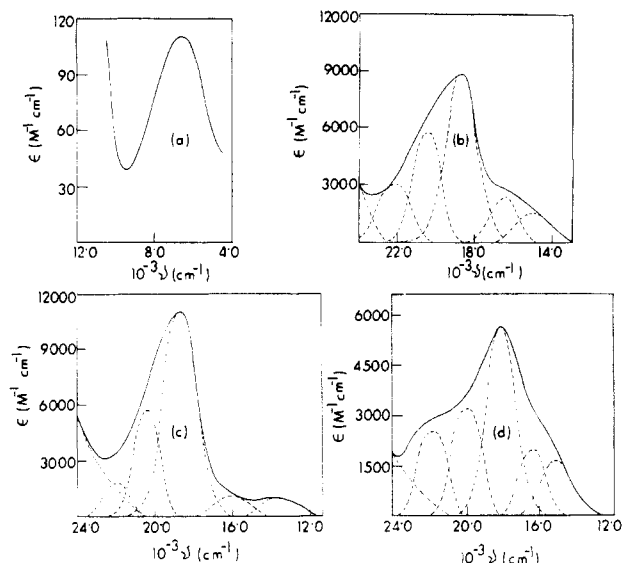

Ru(t$_2$) → azo(π*) back-bonding as reflected in short Ru–N and long N–N distances.[3,5] Associated with such bonding are the red-shift[4,6] of $\nu_{N=N}$ and the display of strong MLCT transitions[2–6]

in the visible region—a property that can be useful in protein labeling via azo functionalization.[7] Also associated is the multiple-electron-transfer activity[2,4] of the chromophore occurring at relatively high potentials—a property that can help in mediating energetic electroprotic transformations such as the oxidation of water to dioxygen.[8]

Such results have encouraged us to explore newer azo–ruthenium chemistry. Ligands examined thus far are mostly[2–6] of the bidentate N,N type where one of the nitrogen atoms is of the azo type. Herein we describe the binding of ruthenium by a group of N(azo),S(thioether) ligands viz., 2-(arylazo)phenyl thioethers. The motive behind this choice was to ascertain the effect of attaching two π-acceptor sites—azo and sulfur[9]—to the same ruthenium center on the nature of the compounds produced. In practice two modes of chelation, N,S (**2**) and C,N,S (**3**, via ortho metalation), are observed with a preponderance of the latter. The spectra, reactions, and structure of selected species including a

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(1) (a) Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. (b) Department of Magnetism, Indian Association for the Cultivation of Science. (c) Jadavpur University.

(2) Chakravarty, A. R.; Chakravorty, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 307. Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 3138. Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1983**, 961.

(3) Chakravarty, A. R.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R.; Ghosh, B. K.; Milagros, T. *Inorg. Chem.* **1983**, *22*, 1892.

(4) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246; **1983**, *22*, 602. Goswami, S.; Mukherjee, R. N.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 2825.

(5) Ghosh, B. K.; Mukhopadhyay, A.; Goswami, S.; Ray, S.; Chakravorty, A. *Inorg. Chem.* **1984**, *23*, 4633. Seal, A.; Ray, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 929.

(6) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600; **1982**, *21*, 1914.

(7) Benson, E. P.; Legg, J. I. *Inorg. Chem.* **1981**, *20*, 2504.

(8) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1288.

(9) Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1981**, 495. Davies, A. R.; Einstein, F. W. B.; Farrell, N. P.; James, B. R. *Inorg. Chem.* **1978**, *17*, 1965. Mereer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480. Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. *Inorg. Chem.* **1972**, *11*, 1280. March, F. C.; Ferguson, G. *Can. J. Chem.* **1971**, *49*, 3590. Fergusson, J. E.; Karran, J. D.; Seevaratnam, S. *J. Chem. Soc.* **1965**, 2627.
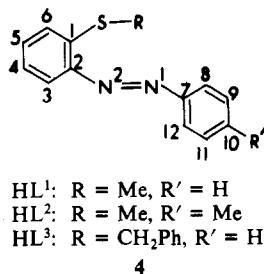
Figure 1. Electronic spectra of (a) coulometrically produced Ru-$(HL^3)(L^3)Cl^+$ in dichloromethane, (b) $Ru(LL)^1$, (c) RuL^1_2, and (d) $Ru(HL^1)(L^1)Cl$. Solid lines in parts b–d are experimental spectra in acetonitrile, and the dotted lines are calculated Gaussian components.

case of novel hexadentate ligation are described. We wish to note that reports on any type of Ru(N,S) coordination are sparse[10] and that the Ru(C,N,S) mode appears to be altogether unknown.

Results and Discussion

A. Syntheses and Two Modes of Ligand Binding. The ligands **4**, prepared[11] by condensing 2-aminophenyl thioethers with nitroso aromatics, are generally abbreviated as HL. Specific abbreviations used are as shown in **4**. Here H refers to the aromatic proton (8-H) that is ionized in the C,N,S coordination mode (see below).

HL^1: $R = Me$, $R' = H$
HL^2: $R = Me$, $R' = Me$
HL^3: $R = CH_2Ph$, $R' = H$

4

When **4** is reacted with ruthenium(III) trichloride trihydrate in boiling methanol, a violet solution is afforded from which a dark solid can be isolated. Chromatography on silica gel affords a blue-violet complex in major yield and a less polar red-violet complex in minor yield. The compositions of the complexes are respectively $Ru(HL)(L)Cl$ and RuL_2. When the above reaction is carried out in the presence of lithium bromide, the products isolated are $Ru(HL)(L)Br$ and RuL_2.

Both types of complexes are diamagnetic, afford nonconducting solutions in polar solvents, and contain ruthenium(II). These show MLCT transitions (Table I, Figure 1) in the visible region, which will be examined further in a latter section.

The RuL_2 species uniformly show (Table I) a single N=N stretch near 1300 cm^{-1}: $Ru(HL)(L)X$ displays two such stretches ($\sim$1370, 1330 cm^{-1}) and a Ru-X stretch near 300 cm^{-1} (X = Cl) or 270 cm^{-1} (X = Br). In the free ligands $\nu_{N=N}$ occur in the range 1450–1475 cm^{-1}. The decrease in $\nu_{N=N}$ on complex formation is characteristic of Ru-azo π-back-bonding.[4,6] The ^{1}H NMR spectrum of RuL_2 in $CDCl_3$ has a single S–Me signal while $Ru(HL)(L)Cl$ affords two equally intense signals (Table II).
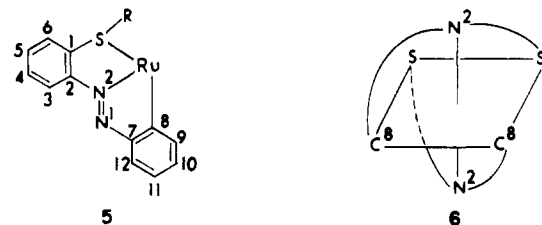
Table I. Selected Infrared and Visible–Ultraviolet Spectral Data

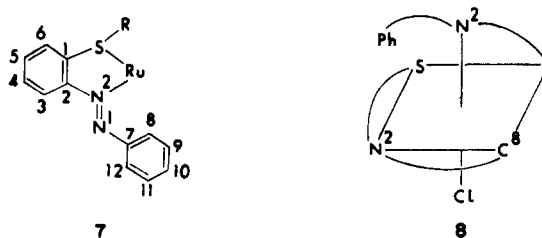| | IR^a ν_{max}, cm^{-1} | | vis–UV^d |
compd	RuX^b	N=N^c	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
RuL^1_2		1290	708 (1000), 532 (11 020), 515 (10 050),^{e} 348 (21 050),^{e} 312 (25 330), 266 (28 350)
RuL^2_2		1290	700 (1140), 533 (10 390), 510 (9110),^{e} 355 (21 410),^{e} 310 (22 000), 257 (26 420)
RuL^3_2		1305	710 (1030), 535 (9660), 515 (8820),^{e} 348 (19 900),^{e} 312 (22 900), 266 (30 700)
$Ru(LL)^1$		1290	708 (1060),^{e} 620 (2570),^{e} 534 (8650), 512 (8100),^{e} 344 (15 610),^{e} 300 (17 550)
$Ru(LL)^2$		1305	700 (1670),^{e} 610 (3390),^{e} 535 (9450), 515 (8790),^{e} 360 (20 860),^{e} 300 (21 750), 285 (22 250), 255 (25 080)
$Ru(LL)^3$		1290	708 (1590),^{e} 620 (2610),^{e} 534 (8010), 515 (7490),^{e} 344 (16 050),^{e} 300 (17 750)
$Ru(HL^1)(L^1)Cl$	303	1370, 1332	650 (2450),^{e} 550 (5660), 480 (3200),^{e} 350 (12 010), 280 (19 100)
$Ru(HL^1)(L^1)Br$	275	1370, 1330	536 (4760), 484 (4050),^{e} 350 (9920),^{e} 288 (15 810)
$Ru(HL^2)(L^2)Cl$	295	1380, 1345	540 (4560), 490 (3790),^{e} 375 (10 850), 285 (16 010)
$Ru(HL^3)(L^3)Cl$	303	1362, 1330	545 (5260), 484 (4670), 360 (12 300),^{e} 285 (20 150)^e
$Ru(HL^3)(L^3)Br$	260	1365, 1330	540 (4850), 480 (4640), 360 (11 400),^{e} 285 (20 540)

^{a}All bands are sharp and strong. ^{b}In polyethylene disk (400–100 cm^{-1}). ^{c}In KBr disk (4000–400 cm^{-1}). ^{d}In acetonitrile. ^{e}Shoulder.

These results suggest that the two ligands are equivalently bonded in RuL_2 and they are inequivalent in $Ru(HL)(L)Cl$.

It will be seen later that the pattern of aromatic ^{1}H resonances in RuL_2 (Table II) is diagnostic of the presence of two chelate rings of type **5** arranged as in **6**. This has been confirmed by

5

6

three-dimensional X-ray work[12] on a partially chlorinated analogue to RuL^3_2, and similar work on the corresponding analogue of $Ru(HL^3)(L^3)Cl$ has revealed the presence of one chelate ring of type **5** and one type **7** arranged as in **8**. The coordination spheres in both cases are distorted-octahedral.

7

8

Virtually all ortho-metalated ruthenium(II) compounds reported in the literature contain soft donors such as carbon monoxide

(10) Root, M. J.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 622.
(11) Shriner, R. L.; Struck, H. C.; Jorison, W. J. *J. Am. Chem. Soc.* **1930**, *52*, 2060. Buraway, A.; Vellins, C. E. *J. Chem. Soc.* **1954**, 90, Livingstone, S. E. *J. Chem. Soc.* **1956**, 437.

(12) Due to an artifact in the synthetic procedure in the early stages of the present work, the crystals (R = CH_2Ph) actually used for the X-ray work were found to be partially ($\sim$25%) chlorinated at 9-C. There is an associated disorder problem and other points of crystallographic interest. Details will be published elsewhere.
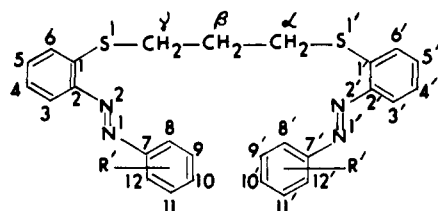
Table II. ¹H NMR Spectral Data[a,b] in CDCl₃

	δ (J, Hz)				
compd	9-H	10-H	11-H	12-H	others
RuL¹₂	6.65 (8)[d]	6.69 (8)[e]	6.87 (8)[e]	8.07 (8)[d]	8.72 (8),[d,f] 7.52[g] 2.09[h,i]
RuL³₂	6.67 (8)[d]	6.70 (8)[e]	6.88 (8)[e]	8.08 (8)[d]	8.67 (8),[d,f] 6.99 (8),[d,j] 7.53 (8),[e,k] 7.30 (8),[e,l] 3.38 (11),[d,m] 3.76 (11)[d,m]
Ru(LL)¹	6.57 (8)[d]	6.72 (8)[e]	6.94 (8)[e]	8.25 (8)[d]	8.88 (8),[d,f] 7.64,[g] 1.78,[n] 2.78,[n] 3.04[n]
Ru(LL)²	6.34[i]		6.74 (8)[d]	8.12 (8)[d]	8.84 (8),[d,f] 7.64,[g] 1.95,[o,j] 1.80,[n] 2.81,[n] 3.06[n]
Ru(LL)³	6.38 (8)[d]	6.50 (8)[d]		8.00[i]	8.78 (8),[d,f] 7.48,[g] 2.24,[p,i] 1.78,[n] 2.78,[n] 3.04[n]

[a] Proton numbering system is as in structures **5-8**, **9**, and *10*. [b] ¹H NMR spectrum of Ru(HL¹)(L¹)Cl. S–Me: 2.70,[i] 3.03.[i] Aromatic protons of the nonmetalated ring: 8- and 12-H, 5.80 (8);[d] 9- and 11-H, 6.72 (8);[e] 10-H, 6.93 (8).[e] Other aromatic protons: 7.09,[c] 7.33,[c] 7.52 (8),[d] 7.58,[c] 7.78 (8),[d] 7.84 (8),[d] 7.92 (8),[d] 8.00 (8).[d] [c] Center of complex pattern due to aromatic protons. [d] Doublet. [e] Triplet. [f] 3-H. [g] Center of overlapping complex pattern representing 4-H, 5-H, and 6-H. [h] S–CH₃. [i] Singlet. [j] 6-H. [k] 4-H. [l] 5-H. [m] Doublet signal due to inequivalent CH₂ protons (confirmed by decoupling experiments) of the benzyl group. [n] Center of complex pattern due to CH₂ protons. [o] 10-CH₃. [p] 11-CH₃.

and/or tertiary phosphines as coligands.[13] The present complexes are notable exceptions—here a soft center (thioether) is built intramolecularly into the main ligand frame. Furthermore, the azo unit is also soft and the arylazo function is sterically well suited to promote ortho metalation. Chelate rings of type **7** in which one azo nitrogen is pendent are rare. The only other example known to us occurs in a nickel(II) complex.[14]
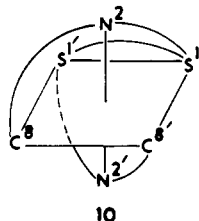
B. Hexadentate Ligation. The formation of the RuL_2 complexes (**6**) led us to consider the possibility that ligands of type **9** (H_2LL) might bind ruthenium(II) in the di-ortho-metalated

$H_2(LL)^1$: R′ = H
$H_2(LL)^2$: R′ = 10-Me, 10′-Me
$H_2(LL)^3$: R′ = 11-Me, 11′-Me
9

hexadentate fashion as in **10**. To our knowledge $C_2N_2S_2$ hexa-

10

dentate ligation of this type is unprecedented. The reaction of ruthenium(III) trichloride trihydrate with **9** indeed affords violet complexes of composition Ru(LL). The synthetic sequence for ligand and complex is in Scheme Ia. Here no blue-violet precursor could be isolated or identified.

The 200-MHz ¹H NMR spectra of the aromatic protons (Table II, Figure 2) are in complete agreement with structure **10** in which the halves of the molecule are equivalent to each other (e.g. **9** ≡ **9′** etc.). The spin–spin structure of the spectrum as the methyl substituent position is systematically varied affords unequivocal assignment of all signals pertaining to the metalated rings. Thus 9-H is a doublet in Ru(LL)¹ and Ru(LL)³ but is a singlet in Ru(LL)². Similarly 12-H is a doublet in Ru(LL)¹ and Ru(LL)²

(13) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3204; **1971**, 2820. Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1325. Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 196. Omae, I. *Chem. Rev.* **1979**, *79*, 287. Jameson, G. B.; Muster, A.; Robinson, S. D.; Wingfield, J. N.; Ibers, J. A. *Inorg. Chem.* **1981**, *20*, 2448. McGuiggan, M. F.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 2523. Patrick, J. M.; White, A. H.; Bruce, M. I.; Beatson, M. J.; Black, D. St. C.; Deacon, G. B.; Thomas, N. C. *J. Chem. Soc., Dalton Trans.* **1983**, 2121. Saunders, D. R.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2133.
(14) Dyachenko, O. A.; Atovmyan, L. O.; Aldoshin, S. M. *J. Chem. Soc., Chem. Commun.* **1975**, 105.
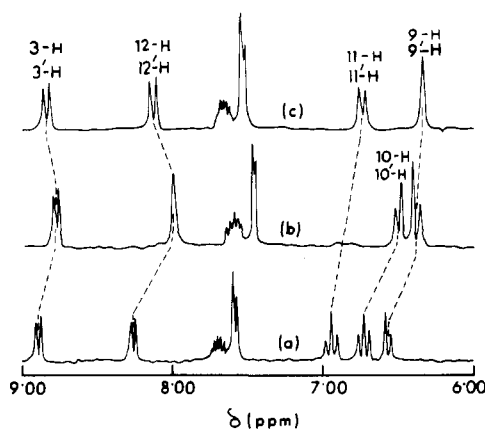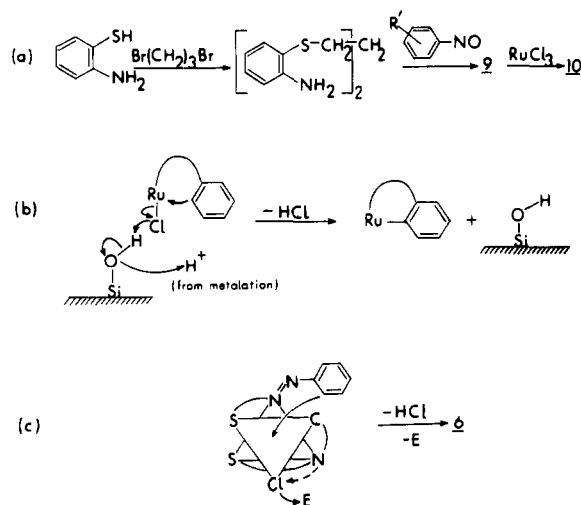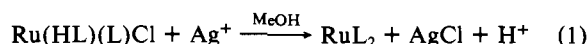
Scheme I

(a), (b), (c)

Figure 2. ¹H NMR spectra of (a) Ru(LL)¹, (b) Ru(LL)³, and (c) Ru(LL)² in the aromatic region. Solvent and the internal standard are CDCl₃ and tetramethylsilane, respectively.
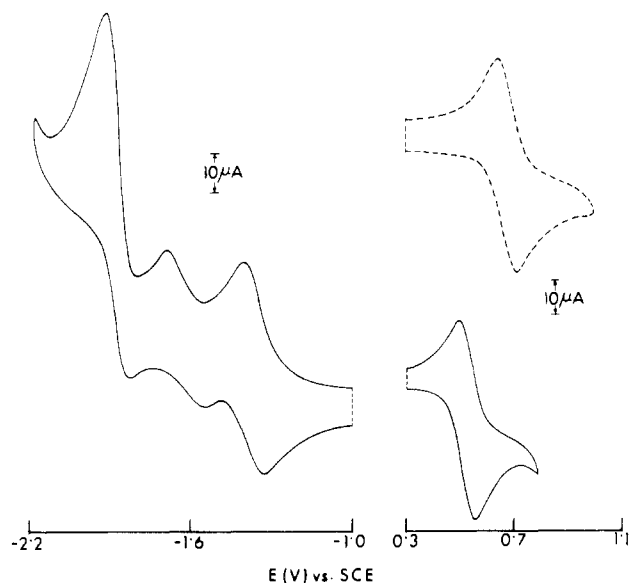
but is a singlet in Ru(LL)³. In all cases the metalation position is fixed at 8-C. For Ru(LL)³, metalation at 12-C would be distinct from that at 8-C. However the complex actually isolated corresponds exclusively to the latter situation in which metalation occurs at the sterically less hindered ortho position. The ¹H NMR spectrum of the RuL_2 species can similarly be used as a proof of structure **6**. On the other hand the spectrum of Ru(HL)(L)Cl is too complex, and only partial assignment is possible (Table II).

C. Reactions. (a) The Second Metalation. In the reaction of **4** with ruthenium(III) trichloride, RuL_2 is formed only as a minor constituent. When a solution of Ru(HL)(L)Cl is boiled in methanol in the presence of silver(I) salts, reaction 1 occurs slowly

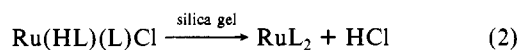$$\text{Ru(HL)(L)Cl} + \text{Ag}^+ \xrightarrow{\text{MeOH}} \text{RuL}_2 + \text{AgCl} + \text{H}^+ \qquad (1)$$

and RuL_2 can be isolated from the reaction mixture though in poor yield ($\sim$15%). Much better conversion ($\geq$60%) is achieved

Figure 3. Cyclic voltammograms of $\sim 10^{-3}$ M Ru(HL^1)(L^1)Cl (- - -) and RuL$^1_2$ (—) in acetonitrile (0.1 M TEAP) at 298 K. Platinum and glassy-carbon working electrodes are respectively used in the positive and negative potential regions.
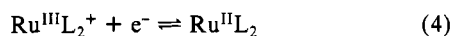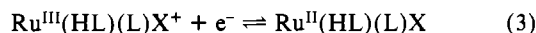
by adsorbing Ru(HL)(L)Cl on silica gel and mildly heating (323 K) the solid mass (eq 2). Only one precedent for this unusual

$$\text{Ru(HL)(L)Cl} \xrightarrow{\text{silica gel}} \text{RuL}_2 + \text{HCl} \qquad (2)$$

reaction, i.e. catalysis of ortho metalation by silica gel surface, is known.[15] Reaction 2 was generally used in the present work for the practical synthesis of RuL$_2$.

The displacement of chloride from Ru(HL)(L)Cl via electrophilic assistance from Ag$^+$ is understandable.[16] In the case of silica gel surface the acidic SiOH protons[17] could provide effectively similar assistance (Scheme Ib). This, however, does not immediately settle the pathway of the conversion **8** → **6** since the aromatic ring to be ortho metalated is located trans to the reactive group (chloride) in **8**. A plausible rationale of the conversion can be facial attack by the pendent aryl group of **8** followed by edge displacement[18] of the nitrogen center of the tridentate ligand with synchronous chloride removal assisted by an electrophile (E) as shown in Scheme Ic.

(b) Metal Oxidation. Complexes **8** and **6** provide an unique opportunity to observe the effect of the displacement of Ru–Cl by Ru–C on the relative ease of metal oxidation. The ruthenium(III)/ruthenium(II) couples 3 and 4 for the various complexes

$$\text{Ru}^{III}(\text{HL})(\text{L})\text{X}^+ + \text{e}^- \rightleftharpoons \text{Ru}^{II}(\text{HL})(\text{L})\text{X} \qquad (3)$$

$$\text{Ru}^{III}\text{L}_2{}^+ + \text{e}^- \rightleftharpoons \text{Ru}^{II}\text{L}_2 \qquad (4)$$
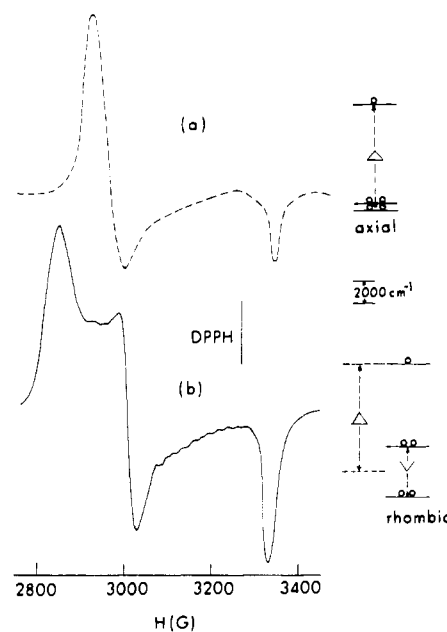
can be readily identified by cyclic or differential-pulse voltammetry in an acetonitrile or a dichloromethane solution at a platinum working electrode (Table III, Figure 3). The couples are reversible to quasi-reversible in nature with peak-to-peak separation (ΔE_p) of 60–120 mV. The one-electron stoichiometry of the couples has been confirmed by coulometry.

The coulometrically produced solutions of Ru(HL)(L)X$^+$ and RuL$_2{}^+$ are respectively yellow-brown and orange. These are however unstable, and isolation of the oxidized complexes in the

(15) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1984**, 999.

(16) Avshu, A.; O'Sullivan, R. D.; Parkins, A. W.; Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1619. Yang, Z.; Young, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2019.

(17) Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, Oxford, England, New York, 1981; p 59.

(18) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 2737. Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391.

Table III. Cyclic Voltammetric Data^{a,b} in Acetonitrile (298 K)

compd	$E^\circ{}_{298}(\Delta E_p)^c$ of Ru(III)–Ru(II)	other responses^d
RuL$^1_2$	0.53 (60)	−1.40, −1.69, −1.91
RuL$^2_2$	0.51 (120)	−1.38 (120),^{e} −1.92 (140)^e
RuL$^3_2$	0.54 (60)^f	−1.29, −1.89
Ru(LL)^1	0.60 (70)	−1.39 (70),^{e} −1.64
Ru(LL)^2	0.60 (60)^g	−1.41 (60)^e
Ru(LL)^3	0.57 (60)	−0.90 (140),^{e} −1.42 (60),^{e} −1.73 (80),^{e} −1.96 (60)^e
Ru(HL^1)(L^1)Cl	0.68 (60)	−1.08, −1.68
Ru(HL^1)(L^1)Br	0.69 (80)	−1.03, −1.60, −2.26
Ru(HL^2)(L^2)Cl	0.67 (120)	−1.13, −1.74
Ru(HL^3)(L^3)Cl	0.69 (70)^h	−1.03, −1.82
Ru(HL^3)(L^3)Br	0.69 (60)	−0.97 (70),^{e} −1.63, −1.80, −1.99

^{a} Meaning and units of symbols are the same as in the text. ^{b} Supporting electrolyte TEAP (0.1 M), solute concentration $\sim 10^{-3}$ M, scan rate 50 mV s^{-1}. ^{c} At platinum working electrode. ^{d} At the glassy-carbon working electrode; unless otherwise mentioned all are cathodic peak potentials (E_{pc}). $^e E^\circ{}_{298}$ (ΔE_p). $^f n = 0.998$; $n = Q/Q'$ where Q' is the calculated coulomb count for 1e transfer and Q is the coulomb count found after exhaustive electrolysis; oxidation was performed at +0.80 V. $^g n = 0.997$; oxidation was performed at 0.85 V. $^h n = 0.991$; oxidation was performed at +0.90 V.

Figure 4. EPR spectra (77 K) of (a) Ru(L^3)$_2{}^+$ and (b) Ru(HL^3)(L^3)Cl$^+$ produced coulometrically in dichloromethane. The computed splitting of the t_2 level in each case is shown on the right-hand side.

pure state has not been possible. The formal potential ($E^\circ{}_{298}$; all potentials referenced to SCE) of couple 3 is 100–150 mV more positive than that of couple 4. Thus RuL$_2$ is more readily oxidized than Ru(HL)(L)X. Part of the reason for this no doubt lies in the decrease of the effective charge of the metal ion in going from Ru–Cl to Ru–C due to strong σ-donation from the carbanion in the latter case. The behavior of the Ru(LL) complexes (couple 5) is similar to that of RuL$_2$. Brown solutions of Ru(LL)$^+$ are unstable.

$$\text{Ru}^{III}(\text{LL})^+ + \text{e}^- \rightleftharpoons \text{Ru}^{II}(\text{LL}) \qquad (5)$$

An irreversible oxidation wave is observed in most complexes as well as in free ligands in the region 1–1.5 V. One or more reduction waves are also observable below −1 V (Table III, Figure 3). These responses are presumably ligand-centered.

D. Electronic Structure of Oxidized Complexes. The reversibility (or quasi-reversibility) of couples 3 and 4 suggests that the gross stereochemistries of ruthenium(II) and ruthenium(III) are alike for each class of complex. The electronic structure of the coulometrically produced ruthenium(III) complexes Ru(HL^3)(L^3)Cl$^+$ and Ru(L^3)$_2{}^+$ were probed with the help of their

Table IV. EPR Data and Derived Parameters[a]

compd	soln no.	g_x	g_y	g_z	p	q	r	K	Δ/λ	V/λ	ϵ_1/λ	ϵ_2/λ
Ru(HL³)(L³)Cl⁺	1	-2.291	-2.173	1.963	0.076	0.997	0.017	1.135	10.205	-4.740	7.876	12.697
	2	-2.291	-2.173	-1.963	0.798	0.602	0.012	1.109	0.096	-0.045	1.468	1.537
Ru(L³)₂⁺	1	-2.213	-2.213	1.965	0.076	0.997	0.000	1.051	9.756	0.000	9.363	10.310
	2	-2.213	-2.213	-1.965	0.799	0.600	0.000	1.099	0.089	0.000	1.473	1.531

[a] Symbols have the same meaning as in the text.

EPR spectra after quick freezing (dichloromethane, 77 K). The two complexes respectively afford model rhombic and axial spectra (Table IV, Figure 4) compatible with the low-spin d⁵ configuration of ruthenium(III).

In an octahedral field, the expected ground state of ruthenium(III) is $^2T_2$ corresponding to the electronic configuration t_2^5. An axial (trigonal or tetragonal) distortion (Δ) splits the one-electron t_2 orbital into a nondegenerate (a or b) and a doubly degenerate (e, consisting[19] of the pair e_+ and e_-) component. Correspondingly the $^2T_2$ state splits into ^2A (or ^2B) and ^2E ($^2E_+$ + $^2E_-$). In the presence of rhombic distortion (V) the e orbital and E state get split. The net effect of Δ, V, and spin-orbit coupling (λ) is to resolve the $^2T_2$ state into three Kramers doublets. Using procedures[20-25] described elsewhere in this paper, we found the observed g values to be compatible with two alternative sets (solutions 1 and 2, Table IV) of the parameters Δ, V, ϵ_1, ϵ_2, K, p, q, and r where ϵ_1 and ϵ_2 are the transition energies within the Kramers doublets, K is a parameter related to the orbital reduction factor (see below) and p, q, and r are the coefficients of the component functions that constitute the ground Kramers doublet.

The correctness of solution 1 for each complex is revealed by their optical spectra in the near-IR region (Figure 1). The ruthenium(III) complexes display relatively weak bands (2000-900 nm) assignable to transitions within the Kramers doublets. Such bands are absent in the ruthenium(II) precursors. Taking[21,24] $\lambda \sim 1000$ cm⁻¹, ϵ_1 and ϵ_2 in the case of Ru(HL³)(L³)Cl⁺ are predicted to be ~8000 and ~13000 cm⁻¹, respectively (solution 1). One of these is indeed observed at ~7000 cm⁻¹ (1450 nm). The other transition cannot be observed since there is a rapid rise in absorption above 10000 cm⁻¹ due to tailing of allowed bands occurring in the visible region. In Ru(L³)₂⁺, ϵ_1 and ϵ_2 are closely spaced near 10000 cm⁻¹. A low-intensity band is clearly seen in this region on the tail of a rising absorption. The agreement between observed spectral energies with those predicted by solution 1 is thus very satisfactory. The positive sign of Δ signifies that the nondegenerate one-electron orbital (a or b) lies above the degenerate orbital (e), and the unpaired electron is located in the former (Figure 4).

In the case of the rejected solution 2, the distortion parameters as well as ϵ_1 and ϵ_2 have very small values and no transitions are predicted in the near-IR region. Each of the two complexes have several kinds of coordinating atoms and the large distortion (solution 1) of the electronic structure from the idealized octahedral situation is not unexpected. It is, however, somewhat surprising that Ru(L³⁺)₂⁺, which has no strict symmetry elements, maintains an *effectively* axial electronic structure.[26]

In the above analysis the admixture of excited states (t_2^4e) in the t_2^5 configuration has not been explicitly considered. Such admixture is partly taken care of by the parameter K, which is related to the orbital reduction factor k by eq 6, where B is the

$$K = (1 + 12B/E_{av})k \qquad (6)$$

Racah parameter and E_{av} is an average excitation energy. Using[21] $B \sim 600$ cm⁻¹ and $E_{av} \sim 30000$ cm⁻¹, we have $K = 1.24k$. The k values of Ru(HL³)(L³)Cl⁺ and Ru(L³)₂⁺ are respectively 0.92 and 0.85. Whereas too much significance should not be attached to k values derived in this manner, we just note that Ru(L³)₂⁺ is expected to have greater electron delocalization than Ru(HL³)(L³)Cl⁺ and this is consistent with the lower k value of the former complex.

Some qualitative comments regarding t_2 splitting in the ruthenium(II) complexes **6**, **8**, and **10** can now be made on the basis of their optical spectra. The free azo ligands absorb strongly at ~400 nm and at shorter wavelengths. On the other hand the complexes show multifeatured absorptions at lower energy, 450-750 nm (Table I, Figure 1). It is logical to assign these to MLCT excitations. The observed features can be resolved into a minimum of five Gaussian components (Figure 1). While meaningful assignment of the components to specific transitions cannot be achieved due to the complexity of the ligand, the spectra clearly require the presence of two or three closely spaced low-lying ligand UMO's above metal OMO's. The latter OMO's are the t_2 orbitals whose splitting pattern should be the same as in the ruthenium(III) counterparts—only the magnitude of splitting should be considerably less due to a decrease in the metal oxidation level. From the energy span of the Gaussian components it is estimated[27] that axial splitting for **6**, **8**, and **10** is <4000 cm⁻¹. This upper limit is indeed very much less than the corresponding splitting in the oxidized complexes (~8500 cm⁻¹).

E. Concluding Remarks. 2-(Arylazo)phenyl thioethers display high affinity for ruthenium(II) and afford novel pseudooctahedral coordination spheres of types RuCN₂S₂Cl (**8**) and RuC₂N₂S₂ (**6**). Even more novel is the behavior of ligand **9**, which would normally be considered as a neutral tetradentate ligand but which in practice displays dianionic hexadenticity due to two ortho metalations (**10**). The species Ru(HL)₂Cl₂, Ru(HL)(L)Cl and RuL₂ would constitute a logical sequence of the ortho-metalative progression (N,S)₂Cl₂, (N,S)(C,N,S)Cl, (C,N,S)₂. Unfortunately we could not get any evidence for the existence of the first member[28] of this series presumably due to the facile nature of the first ortho metalation. For the second ortho metalation, silica gel acts as a very effective catalyst probably due to the electrophilic nature of the surface (SiOH protons).

The ruthenium(III) analogues of RuL₂ and Ru(HL)(L)Cl can be electrogenerated in solution by nearly reversible oxidation of the ruthenium(II) parent species. Ortho metalation makes oxi-

(19) Sugano, S.; Tanabe, Y.; Kamimure, H. *Multiplets of Transition Metal Ions in Crystals*; Academic: New York, 1970; p 131.

(20) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University: London, 1961; p 364. Bleany, B.; O'Brien, M. C. M. *Proc. Phys. Soc., London, Sect. B* **1956**, *69*, 1216.

(21) Hill, N. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 427.

(22) Hudson, A.; Kennedy, M. J. *J. Chem. Soc. A* **1969**, 1116.

(23) Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 615.

(24) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614. Bernhard, P.; Stebler, A.; Ludi, A. *Inorg. Chem.* **1984**, *23*, 2151.

(25) Bhattacharya, S.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 3224. Bhattacharya, S.; Chakravorty, A. *Proc.—Indian Acad. Sci., Chem. Sci.* **1985**, *95*, 159.

(26) We have also examined the EPR spectrum of electrogenerated Ru(L²)₂⁺ (dichloromethane, 77 K). The $g_\perp$ (2.204) and $g_\parallel$ (1.964) values are very close to those of Ru(L³)₂⁺, as expected. On the other hand the spectrum of [Ru(LL)²]⁺ taken under similar conditions is complex (presumably due to decomposition), and we have not been able to understand it.

(27) This estimate is made as follows. The Gaussian components are devided into two equal groups such as 1, 2, 3 and 3, 4, 5 where the numbers represent components in ascending order of energy. The energy difference between the centers of gravity of the two groups is taken as the upper limit of the splitting.

(28) The missing complex would be a logical intermediate in synthesis. The ruthenium(III)/ruthenium(II) formal potential of this complex is expected to be higher than that of Ru(HL)(L)Cl, i.e. >0.7 V ($E°_{298}$ order: Ru(HL)₂Cl₂ > Ru(HL)(L)Cl > RuL₂). Thus the hypothetical Ru(HL)₂Cl₂⁺ ion may be a strong enough oxidant to oxidize the reaction medium during synthesis, thus transforming itself into the ruthenium(II) state which finally appears in the form of Ru(HL)(L)Cl and RuL₂. This may be the rationale for the exclusive synthesis of ruthenium(II) complexes even though the starting material is ruthenium(III) chloride.

dation easier. Thus the RuL$_2$ complexes are oxidized at substantially lower potential than the Ru(HL)(L)Cl complexes. The EPR and near-IR spectra of oxidized complexes show the presence of large electronic distortions. Similar but much smaller distortions probably exist in RuL$_2$ and Ru(HL)(L)Cl and afford multiple MLCT transitions.

Experimental Section

Materials. The purification of RuCl$_3$·3H$_2$O, dinitrogen gas, and solvents and preparation of supporting electrolytes for electrochemical work were done as before.[4] All other chemicals and solvents used for the preparative work were of reagent grade and were used without further purification.

Physical Measurements. Electronic and infrared spectra were recorded by using Hitachi 330 and Perkin-Elmer 783 spectrophotometers, respectively. Electronic spectra of oxidized complexes were taken after rapidly transfering the coulometrically oxidized (at potentials given in Table III) solutions to the spectrophotometric cell. Cyclic voltammetry was performed under a dinitrogen atmosphere with the help of a PAR Model 370-4 electrochemistry system as before.[4] In a three-electrode configuration a Beckman Model 39273 platinum electrode was the working electrode. For controlled-potential coulometry a PAR Model 173 potentiostat, Model 179 digital coulometer, and Model 377A cell system having a platinum-wire-gauge electrode was used. All measurements were made at 298 ± 1 K. The potentials are referenced to a saturated calomel electrode and are uncorrected for junction potential. EPR measurements on oxidized complexes were made with a Varian 109C E-line X-band spectrometer using a quartz Dewar. The coulometrically oxidized solution (in dichloromethane) was quickly transfered to an EPR tube, which was immediately frozen in liquid nitrogen. Spectra were then taken. All spectra were calibrated with the help of DPPH ($g = 2.0037$). The microwave power level was maintained at around 0.2 mW. ^{1}H NMR data were collected in CDCl$_3$ solvent with a Varian XL200 or a Bruker 270 MHz spectrometer. Solution electrical conductivity was measured with a Philips PR9500 bridge at a solute concentration of ~10^{-3} M.

Analysis of EPR Data. All five t$_2$ electrons were explicitly considered.[21] The EPR active ground Kramers doublet is written as in eq 7,

$$\psi_A = p|E_+\rangle + q|\bar{A}\rangle + r|E_-\rangle \qquad \psi_B = p|\bar{E}_-\rangle + q|A\rangle + r|\bar{E}_+\rangle \qquad (7)$$

where states with β-spin are identified by putting a bar on top (depending on the nature of axial symmetry the A representation may have to be replaced by B representation). The three components of the g tensor are

$$g_x = 2[-2pr - q^2 - 2^{1/2}Kq(p + r)] \qquad (8)$$

$$g_y = 2[2pr - q^2 - 2^{1/2}Kq(p - r)] \qquad (9)$$

$$g_z = 2[-p^2 + q^2 - r^2 - K(p^2 - r^2)] \qquad (10)$$

Further details regarding the signs and identification of g_i's and regarding procedures and computational methodologies used for extracting various parameters (Table IV) from observed g values can be found elsewhere.[25]

Gaussian Analysis of Bands. The Gaussian analysis was done by using eq 11[29] where ϵ_ν and ϵ_0 are the extinction coefficients at frequency ν and at band maximum (ν_0), respectively, and δ is the full width at half-height. Fitting was done by trial and error.

$$\epsilon_\nu = \epsilon_0 \exp\left[\frac{-5.545(\nu - \nu_0)^2}{2\delta^2}\right] \qquad (11)$$

Synthesis of Compounds: Ligands of Type HL. 2-(Phenylazo)phenyl methyl thioether (HL^1) was synthesized by condensing *o*-methylthioaniline and nitrosobenzene according to reported procedure.[11]

2-(*p*-Tolylazo)phenyl methyl thioether (HL^2) and 2-(phenylazo)phenyl benzyl thioether (HL^3) were similarly prepared by simply replacing nitrosobenzene by *p*-nitrosotoluene and *o*-methylthioaniline by *o*-benzyl-thioaniline, respectively, in the above procedure.

Ligands of Type H$_2$LL. General Data. The syntheses of all ligands of type H$_2$LL were performed by using a general method. Specific details are given for one representative example.

γ-[2-(Phenylazo)phenylthio]propyl 2-(Phenylazo)phenyl Thioether (H$_2$(LL)^1). 1,3-Bis((2-aminophenyl)thio)propane was first synthesized. Small pieces of metallic sodium (2.8 g, 0.12 mol) were slowly added to a solution of 2-aminothiophenol (15 g, 0.12 mol) in dry ethanol (66 mL). When all the sodium completely dissolved, 1,3-dibromopropane (12.5 g, 0.06 mol) was slowly added and the mixture was refluxed for 2 h. The

(29) Barker, B. E.; Fox, M. F. *Chem. Soc. Rev.* **1980**, *9*, 143.

mass was cooled and poured into cold water (150 mL). The brown oil that separated was extracted with diethyl ether. The ether was evaporated, and the oil was dried with anhydrous Na$_2$SO$_4$. Yield: 12.5 g (72%). The compound so obtained was used without further purification for the next step.

1,3-Bis((2-aminophenyl)thio)propane (2.9 g, 0.01 mol) and nitrosobenzene (2.2 g, 0.02 mol) were dissolved in glacial acetic acid (30 mL). The solution was stirred at 303 K for 2 h. Water (25 mL) was then added. The resulting solution was extracted with petroleum ether (bp 353–373 K). On removal of the solvent in vacuo, the essentially pure ligand was obtained as an orange liquid. Yield: 1.15 g (25%). Anal. Calcd for C$_{27}$H$_{24}$N$_4$S$_2$: C, 69.22; H, 5.13; N, 11.96. Found: C, 69.10; H, 5.18; N, 11.75.

γ-[2-(*p*-Tolylazo)phenylthio]propyl 2-(*p*-tolylazo)phenyl thioether (H$_2$(LL)^2) (yield 30%) was similarly prepared by using *p*-nitrosotoluene instead of nitrosobenzene in the above procedure. Anal. Calcd for C$_{29}$H$_{28}$N$_4$S$_2$: C, 70.15; H, 5.64; N, 11.29. Found: C, 70.30; H, 5.55; N, 11.20.

γ-[2-(*m*-Tolylazo)phenylthio]propyl 2-(*m*-tolylazo)phenyl thioether (H$_2$(LL)^3) (yield 28%) was similarly prepared by simply replacing nitrosobenzene by *m*-nitrosotoluene in the above procedure. Anal. Calcd for C$_{29}$H$_{28}$N$_4$S$_2$: C, 70.15; H, 5.64; N, 11.29. Found: C, 69.90; H, 5.50; N, 11.20.

Preparation of Complexes: Bis[2-(phenylazo)phenyl methyl thioether-*C^8,N^2,S*]ruthenium(II) (RuL^1$_2$) and Chloro[2-(phenylazo)phenyl methyl thioether-*N^2,S*][2-(phenylazo)phenyl methyl thioether-*C^8,N^2,S*]ruthenium(II) (Ru(HL^1)(L^1)Cl). Nitrogen gas was passed for 5 min through a warmed solution of HL^1 (468 mg, 2.05 mmol) in methanol (60 mL). A solution of RuCl$_3$·3H$_2$O (262 mg, 1.00 mmol) in methanol (10 mL) was then added, and the mixture was heated to reflux under nitrogen atmosphere for 4 h. During this period the solution turned violet, and a dark precipitate began to deposit. The solvent was then evaporated to ~10 mL. After the mixture was cooled to room temperature, the precipitate was collected by filtration and washed thoroughly with water and finally with diethyl ether. It was then dried under vacuum over P$_4$O$_{10}$. The dried crude product was dissolved in a small volume of dichloromethane and was subjected to chromatography on a silica gel (BDH, 60–120 mesh) column (30 × 1 cm). An orange band of unreacted ligand was eluted away with benzene.

A red-violet band consisting of RuL^1$_2$ was then eluted. Crystals were obtained by complete evaporation of the benzene eluate. It was finally crystallized from CH$_2$Cl$_2$–CH$_3$CN (1:5) mixture. Yield: 8%. Anal. Calcd for RuC$_{26}$H$_{22}$N$_4$S$_2$: C, 56.19; H, 3.96; N, 10.09. Found: C, 56.10; H, 4.00; N, 10.20.

Following the elution of RuL^1$_2$, the eluant was changed to dichloromethane and a blue-violet band was collected. On evaporation of the solvent a solid mass (350 mg) was obtained. It was ground in an agate mortar with 50 mL of acetonitrile and then stirred at room temperature. This procedure removes traces of adherent RuL^1$_2$. The pure complex was then collected by filtration and was crystallized from dichloromethane–heptane (1:3) mixture. Yield: 335 mg (60%). Anal. Calcd for RuC$_{26}$H$_{23}$N$_4$S$_2$Cl: C, 52.73; H, 3.89; N, 9.46. Found: C, 52.20; H, 3.75; N, 9.45.

Bromo[2-(phenylazo)phenyl methyl thioether-*N^2,S*][2-(phenylazo)-phenyl methyl thioether-*C^8,N^2,S*]ruthenium(II) (Ru(HL^1)(L^1)Br) (yield, 40%) was obtained similarly by using the same reactant stoichiometry and procedure except that LiBr (7 g) was added to the methanolic solution immediately after the addition of RuCl$_3$·3H$_2$O. Anal. Calcd for RuC$_{26}$H$_{23}$N$_4$S$_2$Br: C, 49.05; H, 3.62; N, 8.80. Found: C, 48.85; H, 3.55; N, 8.78. In this procedure a large yield (20%) of RuL^1$_2$ was obtained.

Other RuL$_2$ and Ru(HL)(L)X complexes were obtained similarly by using the appropriate ligands and LiBr where necessary. Analytical data for other complexes prepared similarly are as follows. Anal. Calcd for RuC$_{28}$H$_{26}$N$_4$S$_2$ (RuL^2$_2$): C, 57.61; H, 4.46; N, 9.60. Found: C, 57.23; H, 4.37; N, 9.65. Anal. Calcd for RuC$_{28}$H$_{27}$N$_4$S$_2$Cl (Ru(HL^2)(L^2)Cl): C, 54.22; H, 4.36; N, 9.04. Found: C, 53.92; H, 4.35; N, 9.00. Anal. Calcd for RuC$_{38}$H$_{30}$N$_4$S$_2$ (RuL^3$_2$): C, 64.48; H, 4.24; N, 7.92. Found: C, 63.20; H, 4.35; N, 7.98. Anal. Calcd for RuC$_{38}$H$_{31}$N$_4$S$_2$Cl (Ru-(HL^3)(L^3)Cl): C, 61.32; H, 4.17; N, 7.53. Found: C, 60.93; H, 4.05; N, 7.59. Anal. Calcd for RuC$_{38}$H$_{31}$N$_4$S$_2$Br (Ru(HL^3)(L^3)Br): C, 57.86; H, 3.93; N, 7.11. Found: C, 56.77; H, 3.93; N, 7.32.

[γ-((2-Phenylazo)phenylthio)propyl 2-(phenylazo)phenyl thioether-*C^8,N^2,S^1,C$^{8'}$,N$^{2'}$,S$^{1'}$*]ruthenium(II) (Ru(LL)^1). Dinitrogen gas was passed for 5 min through a warmed solution of H$_2$(LL)^1 (470 mg, 1.00 mmol) in methanol (60 mL). A solution of RuCl$_3$·3H$_2$O (262 mg, 1.00 mmol) in methanol (10 mL) was then added, and the mixture was heated to reflux under nitrogen atmosphere for 4 h and subsequently treated in the same manner as in the synthesis of RuL^1$_2$. From the violet chromatographic band, benzene eluted Ru(LL)^1 was finally obtained. Yield: 115 mg (20%). Anal. Calcd for RuC$_{27}$H$_{22}$N$_4$S$_2$: C, 57.12; H, 3.88; N,

9.87. Found: C, 58.05; H, 3.95; N, 9.50. Here no blue-violet band was eluted by CH_2Cl_2.

The other Ru(LL) complexes were similarly prepared by using the appropriate ligands in the above procedure. Analytical data are as follows. Anal. Calcd for $RuC_{29}H_{26}N_4S_2$ (Ru(LL)^2): C, 58.47; H, 4.37; N, 9.41. Found: C, 58.10; H, 4.30; N, 9.52. Anal. Calcd for $RuC_{29}H_{26}N_4S_2$ (Ru(LL)^3): C, 58.47; H, 4.37; N, 9.41. Found: C, 58.50; H, 4.40; N, 9.37.

Conversion of Ru(HL^1)(L^1)Cl to RuL^1$_2$. **(a) By Silica Gel.** Ru(HL^1)(L^1)Cl (250 mg) was dissolved in dichloromethane (20 mL) and was adsorbed on silica gel (50 g) (BDH, 60–120 mesh). The solvent was removed by evaporation to dryness at room temperature. The dried mass was heated at 323–328 K for 24 h. The red-violet product was then extracted from silica gel with dichloromethane, and the solution was concentrated to ~5 mL. It was subjected to chromatography on a silica gel (BDH, 60–120 mesh) column (30 × 1 cm). A red-violet band was eluted with benzene. On evaporation of the solvent a dark mass deposited. It was crystallized from CH_2Cl_2–CH_3CN (1:5) to yield dark crystals. Yield: 140 mg, (60%).

(b) By Silver(I) Salts. Ru(HL^1)(L^1)Cl (50 mg, 0.08 mmol) was suspended on 20 mL of methanol. To this was added $AgClO_4$ (65 mg, 0.32 mmol), and the mixture was heated to reflux for 30 min. A red-violet solution resulted. After being cooled to room temperature, the solution was filtered through a G4 sintered-glass funnel. The collected solution was evaporated, and the solid mass was subjected to chromatography on a silica gel (BDH, 60–120 mesh) column (15 × 1 cm). A red-violet band eluted with benzene. On evaporation, crystals deposited. These were then dried in vacuum over P_4O_{10}. Yield: 8 mg (17%).

Registry No. RuL^1$_2$, 101377-16-6; RuL^2$_2$, 101377-17-7; RuL^3$_2$, 101377-18-8; Ru(LL)^1, 101402-16-8; Ru(LL)^2, 101377-19-9; Ru(LL)^3, 101377-20-2; Ru(HL^1)(L^1)Cl, 101377-21-3; Ru(HL^1)(L^1)Br, 101377-22-4; Ru(HL^2)(L$_2$)Cl, 101377-23-5; Ru(HL^3)(L^3)Cl, 101377-24-6; Ru(HL^3)(L^3)Br, 101377-25-7; HL^1, 101418-85-3; HL^2, 101418-86-4; HL^3, 101418-87-5; H$_2$(LL)^1, 101418-88-6; H$_2$(LL)^2, 101418-89-7; H$_2$(LL)^3, 101418-90-0; 2-aminothiophenol, 137-07-5; 1,3-dibromopropane, 109-64-8; 1,3-bis((2-aminophenyl)thio)propane, 60435-49-6; nitrosobenzene, 586-96-9; *p*-nitrosotoluene, 623-11-0; *m*-nitrosotoluene, 620-26-8.

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Molten Lithium Sulfate–Sodium Sulfate–Potassium Sulfate Eutectic: Oxidation–Reduction Reactions of Transition-Metal Compounds

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Sulfur dioxide was found to reduce a number of first-row transition-metal compounds in molten ternary sulfate eutectic, the ease of reduction being Cr(VI) > Mn(IV) > Fe(III) > Cu(II). A number of other, probably polymeric, cations (Ti(IV), Nb(V), Mo(VI), Ta(V), W(VI)) were not reduced. Potassium dichromate was unstable, slowly decomposing to chromium(III) oxide, chromate, and oxygen, and was converted to chromate by solutions of sodium carbonate. Chromium metal was little attacked by the ternary eutectic, but copper metal reduced copper(II) to copper(I) cations. Solutions of potassium pyrosulfate decomposed thermally but also oxidized chromium metal (to Cr(III)) and iron(II) (to Fe(III)) and reduced manganese(IV) oxide (to Mn(II)) and chromium(VI) (completely to chromium(III)). Though simple cations (Fe(II), Mn(II)) accelerated the thermal decomposition of pyrosulfate, the more polymeric cations (Ti(IV), Nb(V), Mo(VI), Ta(V), W(VI)) caused considerably less evolution of sulfur trioxide.

Introduction

The systematic study of the chemistry of transition-metal species in molten alkali-metal sulfates is of interest both in its own right as a nonaqueous chemistry and also because of the great practical importance of molten sulfates. Molten sulfates form the reaction films through which the corrosion of high-temperature boilers and heat exchangers occurs and also act as catalysts in the production of sulfuric acid. These catalysts for sulfur dioxide oxidation with air consist of solutions of vanadium, and of other transition metals that act as "promoters", dissolved in molten sulfate and absorbed on kieselguhr.

This paper reports the results of studies of oxidation–reduction reactions of transition-metal compounds, to complement the parallel studies on acidic–basic reactions of these compounds,[1] excluding those of vanadium, which are described elsewhere.[2]

Little has previously been published on oxidation–reduction equilibria in molten sulfates, though there are very brief reports that copper(I) was found to be slowly oxidized to copper(II) (in K_2SO_4–$ZnSO_4$ at 600 °C),[3] possibly by the air atmosphere. However the iron(II)–iron(III) equilibrium (under the same conditions) involved measurable amounts of both oxidation states with a majority of the former.[3] More surprisingly, potassium chromate, under these conditions, was rapidly reduced to chromium(III), which was apparently soluble as spectra were obtained.[3] In contrast, potassium chromate was found to dissolve

to give a red melt of reasonable stability in the ternary eutectic (Li_2SO_4 78%, Na_2SO_4 8.5%, K_2SO_4 13.5%) at 550 °C though it was reduced to chromium(III) by magnesium or thallium. These metals also reduced molybdenum(VI) in the same melt, to molybdenum(IV).[4] In addition it has been mentioned that cobalt(III) compounds rapidly decomposed to cobalt(II),[5] while potassium permanganate[3] and potassium tetrachloroplatinate(II)[6] were reported briefly to decompose to unspecified products (all in K_2SO_4/$ZnSO_4$). Many studies, frequently electrochemical, of the corrosion (oxidation) of transition metals have been reported, but in most cases, in pure sulfate melts, insoluble oxides or sulfides resulted.[4,7–11]

Experimental Section

Materials. The ternary eutectic, sodium carbonate, and potassium pyrosulfate were prepared as previously reported[12] as were the transi-

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(1) Dearnaley, R. I.; Kerridge, D. H.; Rogers, D. J. *Inorg. Chem.* **1985**, *24*, 4254.
(2) Dearnaley, R. I.; Kerridge, D. H. *Thermochim. Acta* **1983**, *63*, 219.
(3) Duffy, J. A.; Macdonald, W. J. D. *J. Chem. Soc. A* **1970**, 977.
(4) Johnson, K. E.; Laitenen, H. A. *J. Electrochem. Soc.* **1963**, *110*, 314.
(5) Duffy, J. A.; Macdonald, W. J. D. *J. Chem. Soc. A* **1971**, 1160.
(6) Duffy, J. A.; Macdonald, W. J. D. *Phys. Chem. Glasses* **1971**, *12*, 87.
(7) Hill, D. G.; Porter, B.; Gillespie, A. S. *J. Electrochem. Soc.* **1958**, *105*, 408.
(8) Bartlett, H. E.; Johnson, K. E. *Can. J. Chem.* **1966**, *44*, 2119.
(9) Burrows, B. W.; Hills, G. J. *Electrochim. Acta* **1970**, *15*, 445.
(10) Cutler, A. J. B. *J. Appl. Electrochem.* **1971**, *1*, 19.
(11) Comtat, M.; Loubet, G.; Mahenc, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *40*, 167.