Tris- and Pentakis-dialkyldithiocarbamates of Ruthenium, $[Ru(S_2CNR_2)_3]^n$ and $[Ru_2(S_2CNR_2)_5]^n$ ($n = +1, 0,$ and -1): Chemical and Electrochemical Interrelations

By **Alan R. Hendrickson, Janet M. Hope,** and **Raymond L. Martin,*** Research School of Chemistry, Australian National University, P.O. Box No. 4, Canberra, Australia 2600

The electron-transfer characteristics of many ruthenium(III) dithiocarbamates have been studied in acetone at a platinum electrode. The tris complexes undergo a relatively facile, reversible, one-electron reduction step to yield the ruthenium(II) complexes $[Ru(S_2CNRR')_3]^-$ (R,R′ = Me, Et, Pr^i, Bu^i, Ph, $PhCH_2$, C_6H_{11}; RR′ = piperidinyl, 2,6-dimethylpiperidinyl, pyrrolidinyl, or morpholinyl). The corresponding one-electron oxidation step to the formally ruthenium(IV) complex $[Ru(S_2CNRR')_3]^-$ is not reversible, the degree of irreversibility being markedly dependent on the substituents R and R′. Substituent effects on the redox potentials parallel those reported previously for many first-row transition-metal dithiocarbamates. Chemical and electrolytic oxidation of $[Ru(S_2CNR_2)_3]$ yield the dimeric ruthenium(III) cations $[Ru_2(S_2CNR_2)_5]^+$ which are obtained in two structural isomeric forms, α and β. Both series (α and β) undergo successive one-electron reductions to the corresponding $[Ru_2(S_2CNR_2)_5]$ and $[Ru_2(S_2CNR_2)_5]^-$ complexes. The rates of isomerisations (i) and (ii) have been measured. The combined redox-

$$\beta\text{-}[Ru_2(S_2CNMe_2)_5]^- \longrightarrow \alpha\text{-}[Ru_2(S_2CNMe_2)_5]^- \qquad \text{(i)}$$

$$\alpha\text{-}[Ru_2(S_2CNMe_2)_5]^+ \longrightarrow \beta\text{-}[Ru_2(S_2CNMe_2)_5]^+ \qquad \text{(ii)}$$

potential data and equilibrium measurements afford the relative thermodynamic stabilities of the six dimeric species. Many of the new complexes have been characterised by spectroscopic techniques including i.r., visible–u.v., and ^1H n.m.r. Paramagnetic shift reagents have been employed and, in the case of $\beta\text{-}[Ru_2(S_2CNMe_2)_5]^+$, enantiomers have been distinguished with an optically active shift reagent.

RUTHENIUM(III) dithiocarbamates have been well characterised by *X*-ray structural [1-3] and ^1H n.m.r. [4-6] studies since they were first reported by Cambi and Malatesta.[7-9] Patterson and Holm [10] suggested that the ruthenium(IV) cation $[Ru(S_2CNMe_2)_3]^+$ should be

---

[1] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and A. M. Venanzi, *Chem. Comm.*, 1966, 476.

[2] L. Pignolet, *Inorg. Chem.*, 1974, **13**, 2051.

[3] (*a*) C. L. Raston and A. H. White, *J.C.S. Dalton*, 1975, 2405; (*b*) *ibid.*, p. 2410.

[4] L. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, 1971, **93**, 360.

[5] L. Pignolet, D. J. Duffy, and L. Que, *J. Amer. Chem. Soc.*, 1973, **95**, 295.

[6] D. J. Duffy and L. Pignolet, *Inorg. Chem.*, 1974, **13**, 2045.

[7] L. Cambi and L. Malatesta, *Ber.*, 1937, **70**, 2067.

[8] L. Cambi and L. Malatesta, *Rend. Ist., Lombardo Sci. Lettre*, 1938, **A181** (*Chem. Abs.*, 1940, **34**, 3201–1).

[9] L. Malatesta, *Gazzetta*, 1938, **68**, 195.

[10] G. S. Patterson and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 2285.

accessible synthetically. They noted that the voltammetry of $[Ru(S_2CNEt_2)_3]$ in *NN*-dimethylformamide (dmf) is characterised by a one-electron oxidation [+0.38 V relative to the standard calomel electrode (s.c.e.)] which differed only slightly from that observed for $[Fe(S_2CNEt_2)_3]$ (+0.42 V). Complexes $[Fe(S_2CNR_2)_3]^+$ have been isolated and characterised.[11,12] Subsequently, the oxidation of $[Ru(S_2CNEt_2)_3]$ by boron trifluoride–air in dry toluene (or benzene) [11] was reported to yield a diamagnetic oligomer ($n = 2.6$), although no structural formulation was proposed.[13] In fact, the dark red benzene-insoluble oligomer was shown by *X*-ray crystallography [14] to be $[Ru_2(S_2CNEt_2)_5]$ $[BF_4]$ confirming that oxidation of a ligand and not the metal atom had occurred.

Two types of bridging dithiocarbamate ligand occur in the dimeric cation and the relatively short Ru · · · Ru distance (2.74 Å) reveals the presence of a metal–metal bond. This finding is in marked contrast to that reported [15-17] for the structures of the related bimetallic cations $[Co_2(S_2CNEt_2)_5]^+$ and $[Rh_2(S_2CNMe_2)_5]^+$, which are characterised by only one type of dithiocarbamate bridge and the absence of a metal–metal bond (Co · · · Co 3.372, Rh · · · Rh 3.556 Å). Furthermore, the absolute configurations of the octahedral environment of the two cobalt (or rhodium) atoms are opposed (Δ and Λ chiralities) whereas in $[Ru_2(S_2CNEt_2)_5]$ $[BF_4]$ they are the same. Recently, Raston and White [3] isolated, from metathesis of aqueous solutions of ' ruthenium trichloride trihydrate ' and sodium dialkyldithiocarbamate, red materials which, after recrystallisation, yielded the bimetallic solvated species $[Ru_2(S_2CNPr^i_2)_5]Cl\cdot 2.5C_6H_6$ and $[Ru_2(S_2CNPr^i_2)_5][Ru_2Cl_6]\cdot 2CHCl_3\cdot(C_6H_6?)$. Both cations, unlike that of Pignolet and Mattson,[14] possess the same stereochemistry as that of the $[Co_2(S_2CNEt_2)_5]^+$ archetype.[16]

Aspects of the chemistry of ruthenium dithiocarbamates are developed in this paper, namely the redox behaviour of $[Ru(S_2CNR_2)_3]$ and of the two bimetallic

$$[Ru(S_2CNR_2)_3]^+ \overset{e^-}{\rightleftharpoons} [Ru(S_2CNR_2)_3] \overset{e^-}{\rightleftharpoons} [Ru(S_2CNR_2)_3]^- \quad (1)$$

isomeric forms of $[Ru_2(S_2CNR_2)_5]^+$.

$$[Ru_2(S_2CNR_2)_5]^+ \overset{e^-}{\rightleftharpoons} [Ru_2(S_2CNR_2)_5] \overset{e^-}{\rightleftharpoons} [Ru_2(S_2CNR_2)_5]^- \quad (2)$$

EXPERIMENTAL

Electronic spectra were obtained on a Cary 14 spectrometer and i.r. spectra, obtained on a Perkin-Elmer 457 instrument, were recorded in KBr discs or KBr solution cells. Qualitative ^1H n.m.r. spectra were obtained with a JEOL 100-MHz instrument, a Varian HA-100 spectrometer being used for quantitative and shift-reagent measurements.

Electrochemical.—All the measurements were made with a three-electrode Princeton Applied Research model 170 instrument with platinum working and auxiliary electrodes. Unless otherwise noted, measurements were made on *ca.* 10^{-3} mol dm^{-3} depolariser in 0.1 mol dm^{-3} $[NEt_4][ClO_4]$–Me_2CO solutions with potentials referred to a Ag–AgCl–0.1 mol dm^{-3} LiCl–Me_2CO electrode.[18] The phase-sensitive a.c. voltammograms were measured in phase with the input alternating potential. An a.c. potential (80 Hz) of 5 mV peak to peak and a scan rate of 10 mV s^{-1} were used unless noted otherwise. Cyclic voltammograms at scan speeds greater than 200 mV s^{-1} were displayed on a Tektronix 5031 storage oscilloscope and recorded on Polaroid film. Coulometry, electrolysis, and spectral monitoring of electrolysed solutions were carried out in vessels of our own design.[19]

Preparation of Complexes.—The assignment of isomers as α or β is described in the Results and Discussion section.

Tris(*dimethyldithiocarbamato*)*ruthenium*(III), $[Ru(S_2CNMe_2)_3]$. *Method A*. Ruthenium trichloride (Johnson, Matthey) (1 g) in water (200 cm^3) was added dropwise with vigorous stirring to $Na[S_2CNMe_2]$ (Eastman Kodak) (2.9 g) in water (200 cm^3) at room temperature. The water-washed precipitate was purified by column chromatography on alumina (neutral) with CH_2Cl_2 as eluant. The complex was recrystallised from CH_2Cl_2–MeOH, yield 0.5 g.

Method B. Preparation *A* above was repeated using water–methanol (1 : 2) and the product which was isolated on addition of water (500 cm^3) was worked-up as described above to give $[Ru(S_2CNMe_2)_3]$ (0.2 g) as a CH_2Cl_2 solvate (Found: C, 21.7; H, 4.0; N, 7.3. $C_{10}H_{20}Cl_2N_3RuS_6$ requires C, 21.9; H, 3.7; N, 7.7%).

α-*Pentakis*(*dimethyldithiocarbamato*)*diruthenium*(III) *Chloride*, α-$[Ru_2(S_2CNMe_2)_5]Cl$. When a sample of $[Ru(S_2CNMe_2)_3]$ as described in *A* or *B* above was prepared, chromatographed, and handled at temperatures at or below room temperature (*ca.* 20 °C), pure samples of α-$[Ru_2(S_2CNMe_2)_5]Cl$ could be obtained by eluting (MeOH) the product after removal of $[Ru(S_2CNMe_2)_3]$. The diruthenium complex was isolated from the concentrated MeOH solution by addition of OEt_2, yields from both preparations *ca.* 0.6 g (Found: C, 20.9; H, 3.7; Cl, 4.1; N, 8.1. $C_{15}H_{30}ClN_5Ru_2S_{10}$ requires C, 21.5; H, 3.6; Cl, 4.2; N, 8.4%).

α-*Pentakis*(*dimethyldithiocarbamato*)*diruthenium*(III) *tetrafluoroborate*, α-$[Ru_2(S_2CNMe_2)_5][BF_4]$. Sodium tetrafluoroborate (0.02 g) was added to α-$[Ru_2(S_2CNMe_2)_5]Cl$ (0.2 g) in MeOH (15 cm^3) and the solution was stirred for 10 min. The precipitated red crystalline complex was recrystallised from acetone–light petroleum (b.p. 80—100 °C) as an acetone solvate (Found: C, 22.8; H, 3.9; N, 7.5. $C_{18}H_{36}BF_4N_5ORu_2S_{10}$ requires C, 22.8; H, 3.8; N, 7.4%).

α-*Pentakis*(*dimethyldithiocarbamato*)*diruthenium*(III) *hexafluorophosphate*, α-$[Ru_2(S_2CNMe_2)_5][PF_6]$. Sodium hexafluorophosphate (0.09 g) in MeOH (3 cm^3) was added with stirring to a solution of α-$[Ru_2(S_2CNMe_2)_5]Cl$ (0.4 g) in MeOH (30 cm^3). The product, which formed immediately, was collected and recrystallised from CH_2Cl_2–MeOH (Found: C, 19.0; H, 3.7; N, 7.2. $C_{15}H_{30}F_6N_5PRu_2S_{10}$ requires C, 19.0; H, 3.2; N, 7.4%).

---

[11] E. A. Pasek and D. K. Straub, *Inorg. Chem.*, 1972, **11**, 259.

[12] R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, 1975, **14**, 1894.

[13] L. Gahan and M. J. O'Connor, *J.C.S. Chem. Comm.*, 1974, 67.

[14] L. H. Pignolet and B. M. Mattson, *J.C.S. Chem. Comm.*, 1975, 49. We thank Professor Pignolet for communicating a fuller account of this work prior to publication.

[15] A. R. Hendrickson and R. L. Martin, *J.C.S. Chem. Comm.*, 1974, 873.

[16] A. R. Hendrickson, R. L. Martin, and D. Taylor, *J.C.S. Dalton*, 1975, 2182.

[17] A. R. Hendrickson, R. L. Martin, and D. Taylor, *Austral. J. Chem.*, 1976, **29**, 269.

[18] A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Electrochem. Soc.*, 1972, **119**, 1325.

[19] A. R. Hendrickson and R. L. Martin, unpublished work.

Conversion of isomers. (*i*) α-[$Ru_2(S_2CNMe_2)_5$]Cl into β-[$Ru_2(S_2CNMe_2)_5$]Cl. The complex α-[$Ru_2(S_2CNMe_2)_5$]Cl was heated under reflux in a minimum volume of MeOH for 8 h. On cooling, crystals of β-[$Ru_2(S_2CNMe_2)_5$]Cl separated (Found: C, 20.7; H, 4.1; Cl, 3.9; N, 7.9. $C_{15}H_{30}ClN_5Ru_2S_{10}$ requires C, 21.5; H, 3.6; Cl, 4.2; N, 8.4%).

(*ii*) α-[$Ru_2(S_2CNMe_2)_5$]X into β-[$Ru_2(S_2CNMe_2)_5$]X (X = BF_4 *or* PF_6). These conversions were undertaken in $CDCl_3$ at *ca.* 60 °C and the reaction was monitored by ^1H n.m.r. spectra. The β-[$Ru_2(S_2CNMe_2)_5$]$^+$ salts were not isolated from these reactions.

β-*Pentakis(dimethyldithiocarbamato)diruthenium*(III) *tetrafluoroborate,* β-[$Ru_2(S_2CNMe_2)_5$][BF_4]. The salt Na[BF_4] (0.03 g) in a minimum volume of MeOH was added to β-[$Ru_2(S_2CNMe_2)_5$]Cl (0.2 g) in MeOH (50 cm^3) and the mixture shaken for a few minutes. On evaporation to dryness *in vacuo* the product was extracted into CH_2Cl_2. The [BF_4]$^-$ salt of [$Ru_2(S_2CNMe_2)_5$]$^+$ was eluted from an alumina column with acetone. The complex may be recrystallised from CH_2Cl_2–OEt_2 or CH_2Cl_2–MeOH (Found: C, 20.9; H, 3.9; N, 7.9. $C_{15}H_{30}BF_4N_5Ru_2S_{10}$ requires C, 20.2; H, 3.4; N, 7.9%).

β-*Pentakis(dimethyldithiocarbamato)diruthenium*(III) *tetrafluoroborate,* β-[$Ru_2(S_2CNMe_2)_5$][BF_4]. Diethyl ether–boron trifluoride (2 cm^3 of 45% solution in OEt_2) was added to [$Ru(S_2CNMe_2)_3$] (0.46 g) in warm benzene (50 cm)^3 with stirring, whereupon a red oil formed which yielded dark red crystals of the complex from acetone on addition of OEt_2 and cooling (Found: C, 19.9; H, 3.4; B, 1.2; F, 8.7; N, 7.6. $C_{15}H_{30}BF_4N_5Ru_2S_{10}$ requires C, 20.2; H, 3.4; B, 1.2; F, 8.5; N, 7.9%).

Pentakis(dimethyldithiocarbamato)diruthenium, [$Ru_2(S_2CNMe_2)_5$]. All manipulations were made under an inert atmosphere (N_2) and all solutions were degassed.

(*a*) *Electrolytic reduction of* β-[$Ru_2(S_2CNMe_2)_5$][BF_4]. The salt β-[$Ru_2(S_2CNMe_2)_5$][BF_4] (135 mg) was dissolved in acetone and 0.1 mol dm^{-3} [NEt_4][ClO_4] (*ca.* 20 cm^3) and reduced at —0.50 V *versus* Ag–AgCl at a platinum electrode. The neutral product which precipitated was collected, washed quickly with degassed acetone, and dried *in vacuo*.

(*b*) Na[BH_4] *Reduction of* β-[$Ru_2(S_2CNMe_2)_5$]Cl. The salt β-[$Ru_2(S_2CNMe_2)_5$]Cl (0.15 g) was dissolved in degassed MeOH (20 cm^3). Sodium tetrahydridoborate (0.007 g) in MeOH (1 cm^3) was added dropwise with stirring under nitrogen. The dark precipitated product was collected and dried *in vacuo* (Found: C, 22.5; H, 4.1; N, 8.2. $C_{15}H_{30}N_5Ru_2S_{10}$ requires C, 22.4; H, 3.8; N, 8.7%).

Electrolytic oxidation of [$Ru(S_2CNMe_2)_3$]. The complex (0.5 g) in 0.1 mol dm^{-3} [NEt_4][BF_4]–Me_2CO (20 cm^3) was electrochemically oxidised at +0.8 V *versus* Ag–AgCl. The resulting solution was evaporated to dryness at room temperature (*ca.* 20 °C) and the [NEt_4][BF_4] was removed by repeated washing with water. The remaining solid was extracted into CH_2Cl_2 and the solution was dried over magnesium sulphate. The product was then purified by column chromatography on alumina. Elution with CH_2Cl_2 removed [$Ru(S_2CNMe_2)_3$]. Subsequent elution with acetone removed α-[$Ru_2(S_2CNMe_2)_5$][BF_4]. Products were identified by comparing their redox potentials and ^1H n.m.r. spectrum {[$Ru_2(S_2CNMe_2)_5$][BF_4] only} with those of authentic samples.

β-*Pentakis(diethyldithiocarbamato)diruthenium*(III) *tetrafluoroborate,* β-[$Ru_2(S_2CNEt_2)_5$][BF_4]. This complex was prepared in many ways and only one method will be described in detail.

Method A. The complex [$Ru(S_2CNEt_2)_3$] (0.25 g) in benzene (25 cm^3) was cooled in ice until some benzene solidified, whence BF_3 gas was bubbled through the solution for 30 s. After a few minutes the solution was decanted from the red oil which formed. Recrystallisation from acetone by addition of OEt_2 and cooling afforded dark red crystals of the complex (Found: C, 29.0; H, 5.2; B, 1.1; F, 7.2; N, 6.6. $C_{25}H_{50}BF_4N_5Ru_2S_{10}$ requires C, 29.1; H, 4.9; B, 1.1; F, 7.4; N, 6.8%).

The same complex, as determined by ^1H n.m.r. spectra, was formed in the following reactions: (*B*), reaction (*A*) at *ca.* 30 °C; (*C*), reaction (*A*) with BF_3 (g) replaced with $OEt_2 \cdot BF_3$ at room temperature; (*D*), reaction (*A*) at the reflux temperature of benzene; and (*E*), reaction (*A*) with O_2 bubbled through the solution for 2 min prior to and after addition of BF_3 (g).

β-*Pentakis(diethyldithiocarbamato)diruthenium*(III) *chloride* β-[$Ru_2(S_2CNEt_2)_5$]Cl. The products from the 1 : 3 mixture of $RuCl_3$ and [S_2CNEt_2]$^-$ were separated by column chromatography on SiO_2. After elution with CH_2Cl_2 to remove [$Ru(S_2CNEt_2)_3$], the diruthenium complex was eluted with EtOH and was recrystallised from C_6H_6–CH_2Cl_2–OEt_2 as red crystals (Found: C, 31.2; H, 5.1; Cl, 3.3; N, 8.8. $C_{25}H_{50}ClN_5Ru_2S_{10}$ requires C, 30.7; H, 5.1; Cl, 3.6; N, 7.2%).

Pentakis(dibenzyldithiocarbamato)diruthenium(III) *chloride,* [$Ru_2\{S_2CN(CH_2Ph)_2\}_5$]Cl. The complex [$Ru_2\{S_2CN(CH_2Ph)_2\}_5$]Cl was isolated from the mixture of products obtained in reaction of $RuCl_3$ and [$S_2CN(CH_2Ph)_2$]$^-$,by column chromatography on SiO_2. Elution with acetone–benzene (1 : 1) removed [$Ru\{S_2CN(CH_2Ph)_2\}_3$]. Elution with EtOH removed the diruthenium fraction which was recrystallised from CH_2Cl_2–C_6H_6 (Found: C, 56.0; H, 4.7; Cl, 2.1; N, 4.3. $C_{75}H_{70}ClN_5Ru_2S_{10}$ requires C, 56.3; H, 4.4; Cl, 2.2; N, 4.4%).

RESULTS AND DISCUSSION

Reduction of [$Ru(S_2CNR_2)_3$].—Voltammetric reduction data for the series of [$Ru(S_2CNR_2)_3$] complexes are provided in Table 1. The process has been characterised as (3) for R = Me and appears to be appropriate for all the

$$[Ru(S_2CNR_2)_3] + e^- \rightleftharpoons [Ru(S_2CNR_2)_3]^- \qquad (3)$$

other 11 substituents examined. For [$Ru(S_2CNMe_2)_3$], exhaustive electrolysis produced an orange-red solution of [$Ru(S_2CNMe_2)_3$]$^-$ and afforded an *n* value of 1.0. This complex anion undergoes reversible oxidation (by cyclic voltammetry) at an a.c. E_p value coincident with the reduction potential of [$Ru(S_2CNMe_2)_3$]. The ion [$Ru(S_2CNMe_2)_3$]$^-$, being analogous to the [$Fe(S_2CNR_2)_3$]$^-$ species reported recently,[12,20] reacted rapidly with atmospheric oxygen, reverting to [$Ru(S_2CNMe_2)_3$]. Spectral monitoring of the electrolytic reduction of [$Ru(S_2CNMe_2)_3$] in CH_2Cl_2 saturated with [NEt_4][ClO_4] shows the growth of the spectrum of [$Ru(S_2CNMe_2)_3$]$^-$ (Table 2) with well defined isosbestic points at 557 and 413 nm.

Oxidation of [$Ru(S_2CNR_2)_3$].—The electrochemical oxidation of [$Ru(S_2CNR_2)_3$] species is generally not reversible by cyclic voltammetry at 200 mV s^{-1} (Table 3). However, there is a marked substituent

---

[20] J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, 1973, **12**, 2730.

dependence on the degree of reversibility; *e.g.* the pyrrolidinyl derivative $[Ru(S_2CNR_2)_3]$ showed no current on the return cathodic sweep whilst $[Ru(S_2CNMePh)_3]$ had an $i_p{}^f/i_p{}^r$ value of 1.1 at a scan rate of 100 mV s^{-1}.

TABLE 1

Parameters for the reduction of $[Ru(S_2CNRR')_3]$

Complex		A.c. voltammetry			Cyclic voltammetry		
R	R′	E_p/V	$\Delta E^{\frac{1}{2}}$/mV	i_p/c/mA dm^3 mol^{-1}	$i_p{}^f/i_p{}^r$ [a]	ΔE_p [a]/mV	$i_p{}^f/cv^{\frac{1}{2}}$ (av.) [b]/mA s$^{\frac{1}{2}}$ dm^3 mol^{-1} mV$^{-\frac{1}{2}}$
Pr^i	Pr^i	−0.726	93	48	0.9	66	6.2
2,6-Dimethylpiperidinyl		−0.675	*c*	*c*	*c*	*c*	*c*
Bu^i	Bu^i	−0.686	93	48	0.9	63	6.2
Piperidinyl		−0.635	93	44	0.9	62	5.6
Et	Et	−0.656	95	52	0.9	63	6.2
Me	Me	−0.611	94	51	0.9	60	6.1
Et	Ph	−0.559	98	37	0.9	65	5.4
Me	Ph	−0.512	94	33	0.9	65	4.3
Pyrrolidinyl		−0.640	95	36	1.0	64	4.6
Morpholinyl [d]		−0.519	100	28	1.3	65	5.4
$PhCH_2$	$PhCH_2$	−0.481	94	45	0.9	63	5.4
C_6H_{11}	C_6H_{11}	−0.721	93	*c*	*c*	63	*c*

By normal pulse voltammetry the reduction processes showed a reduction potential in good agreement with the E_p results from a.c. voltammetry. $E^{\frac{1}{4}} - E^{\frac{3}{4}}$ Values all fell in the range 53—55 mV and the limiting-current values ranged from 111 to 183 mA dm^3 mol^{-1}.

[a] Scan rate, 100 mV s^{-1}. [b] Average value for v = 20, 50, 100, and 200 mV s^{-1}. [c] Too insoluble for reliable data. [d] Solvate having 2.5 $CHCl_3$.

TABLE 2

Electronic spectra of some ruthenium dithiocarbamates

Complex	Absorption wavelength (nm) [a]					Solvent
$[Ru(S_2CNMe_2)_3]$		558 (3.18)	464 (3.38)	399 (sh)	362 (3.92)	CH_2Cl_2 sat. with $[NEt_4][ClO_4]$
$[Ru(S_2CNMe_2)_3]^-$			468 (3.86)	370 (3.55)	350 (3.57)	
α-$[Ru_2(S_2CNMe_2)_5]^+$	*ca.* 1 000 (2.1) [b]		448 (3.66)		330 (4.32)	Me_2CO
β-$[Ru_2(S_2CNMe_2)_5]^+$	945 (2.26) [b]	553 (3.08)	465 (3.53)	400 (3.83)	327 (4.53)	Me_2CO
α-$[Ru_2(S_2CNMe_2)_5]$ [c]			446		357	CH_2Cl_2 sat. with $[NBu_4][ClO_4]$
β-$[Ru_2(S_2CNMe_2)_5]$ [c,d]	654	577, 510			361	

[a] Values of log ε are given in parentheses. [b] Solvent CH_2Cl_2. [c] Peak positions of electrolytically reduced solutions of α- and β-$[Ru_2(S_2CNMe_2)_5]^+$. [d] No strong peaks ($\varepsilon > 100$ dm^3 mol^{-1} cm^{-1}) in the 700—2 000 nm region.

TABLE 3

Parameters for the oxidation of $[Ru(S_2CNRR')_3]$

Complex		A.c. voltammetry			Cyclic voltammetry [a]	
R	R′	E_p/V	$\Delta E^{\frac{1}{2}}$/mV	i_p/c/mA dm^3 mol^{-1}	ΔE_p [b]/mV	$i_p{}^f/cv^{\frac{1}{2}}$ (av.) [c]/mA s$^{\frac{1}{2}}$ dm^3 mol^{-1} mv$^{-\frac{1}{2}}$
Pr^i	Pr^i	0.476	110	13	113	6.2
2,6-Dimethylpiperidinyl		0.510	*d*	*d*	*d*	*d*
Bu^i	Bu^i	0.539	102	14	105	6.4
Piperidinyl		0.558	104	13	108	5.6
Et	Et	0.565	98	21	118	6.9
Me	Me	0.586	101	18	125	6.5
Et	Ph	0.611	110	18	90	4.9
Me	Ph	0.614	108	13	118	4.1
Pyrrolidinyl		0.589	106	13	99	4.7
Morpholinyl [e]		0.644	100	12	95	3.6
$PhCH_2$	$PhCH_2$	0.666	106	10	119	5.4
C_6H_{11}	C_6H_{11}	0.475	98	*d*	100	*d*

By normal pulse voltammetry the oxidation potentials ($E^{\frac{1}{2}}$) were in good agreement with the E_p results from a.c. voltammetry. $E^{\frac{3}{4}} - E^{\frac{1}{4}}$ Values fell in the range 45—65 mV and the limiting current values ranged from 91 to 156 mA dm^3 mol^{-1}.

[a] The oxidation processes are irreversible with $i_p{}^r$ being only a fraction of $i_p{}^f$ at a scan rate of 100 mV s^{-1}. [b] Scan rate 100 mV s^{-1}. [c] Average value for v = 20, 50, 100, and 200 mV s^{-1}. [d] Too insoluble for reliable data. [e] Solvate having 2.5 $CHCl_3$.

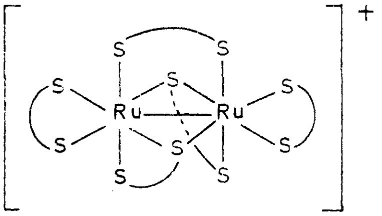
Other substituents examined showed intermediate behaviour. The data for $[Ru(S_2CNMePh)_3]$ suggest that the electrode process is (4) with the formally ruthen-

$$[Ru(S_2CNR_2)_3] \rightleftharpoons [Ru(S_2CNR_2)_3]^+ + e^- \quad (4)$$

ium(IV) species exhibiting various degrees of instability to further reaction or decomposition depending on the substituents. On exhaustive oxidative electrolysis of $[Ru(S_2CNMe_2)_3]$ the resulting solution did not contain $[Ru(S_2CNMe_2)_2]^+$ (cyclic and a.c. voltammetry). When this solution was worked-up by chromatography (see Experimental section) $[Ru(S_2CNMe_2)_3]$ and a diruthenium complex $[Ru_2(S_2CNMe_2)_5]^+$ were isolated although neither species was present originally in the oxidised solution.

For both oxidation and reduction, the effect of substituents on the redox potential is virtually identical to that described for many first-row transition-metal complexes,[12,21-23] with the dibenzyl-substituted complexes being the most difficult to oxidise and the α-branched substituents di-isopropyl and dicyclohexyl providing the complexes which are the easiest to oxidise. The reverse order holds for reduction, with the difference between the oxidation and reduction potentials for any substituent being approximately constant at *ca.* 1.19 V.

Diruthenium Isomers of the Type $[Ru_2(S_2CNR_2)_5]^+$.—The diruthenium species $[Ru_2(S_2CNMe_2)_5]^+$ generated by the electrochemical oxidation of $[Ru(S_2CNMe_2)_3]$ solutions can also be synthesised by chemical methods. This dimer was obtained when solutions of $RuCl_3$ and $[S_2CNMe_2]^-$ were mixed and is readily separated from $[Ru(S_2CNMe_2)_3]$ by chromatography. Metathetical reaction of this chloride salt with $Na[BF_4]$ or $Na[PF_6]$ in methanol afforded the corresponding $[BF_4]^-$ or $[PF_6]^-$ salt. Hydrogen-1 n.m.r. spectra (see later) confirm that the product of electrochemical oxidation and the chemically prepared species are identical. A single-crystal *X*-ray study of α-$[Ru_2(S_2CNMe)_5][PF_6]$ reveals [24] that this species has the same basic structure as described earlier [16,17] for the cobalt(III) and rhodium(III) bimetallic complexes $[Co_2(S_2CNEt_2)_5][BF_4]$ and $[Rh_2(S_2CNMe_2)_5][BF_4]$, *i.e.* as in (I). The ion α-$[Ru_2(S_2CNMe_2)_5]^+$ is diamagnetic (^1H n.m.r. evidence) and possesses a Ru–Ru bond (Ru ··· Ru 2.787 Å), an important feature not exhibited by the low-spin d^6 α complexes of Co^{III} or Rh^{III}. The structure of $[Ru_2(S_2CNMe_2)_5][BF_4]$ represents the third structural determination of this class of ruthenium(III) compound,[36] although this is the first time that many of the physicochemical properties of the complex have been described. The complete *X*-ray structure [24] of the second isomer (β) has also been completed in these laboratories and allows the definite assignment of this isomer. A diethyl derivative has also been characterised by *X*-ray crystallography as the β isomer.[14,*]



β-$[Ru_2(S_2CNMe_2)_5]^+$

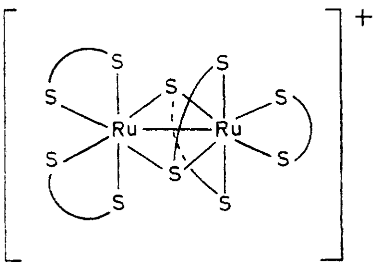
(II)

TABLE 4

Selected spectroscopic data for ruthenium dithiocarbamates

Complex	Solvent for n.m.r.	δ [a]/p.p.m.	ν(C ··· N) Infrared absorptions (cm⁻¹) KBr disc	ν(C ··· N) Infrared absorptions (cm⁻¹) CH_2Cl_2 solution
α-$[Ru_2(S_2CNMe_2)_5][BF_4]$	CD_2Cl_2	2.91, 3.16, 3.45, 3.49, 3.54	1 535 [b]	
β-$[Ru_2(S_2CNMe_2)_5]]BF_4]$	CD_2Cl_2	3.11, 3.20, 3.49, 3.52, 3.55	1 540 [b]	
α-$[Ru_2(S_2CNMe_2)_5]Cl$	CD_2Cl_2	2.92, 3.16, 3.43, 3.47, 3.54	1 530	1 540
β-$[Ru_2(S_2CNMe_2)_5]Cl$	CD_2Cl_2	3.14, 3.19, 3.52(2), 3.55	1 540	1.542
α-$[Ru_2(S_2CNMe_2)_5][PF_6]$	CD_2Cl_2	2.91, 3.16, 3.45, 3.49, 3.54	1 542 [c]	
β-$[Ru_2(S_2CNMe_2)_5][PF_6]$	CD_2Cl_2	3.06, 3.16, 3.44, 3.48, 3.51		
α-$[Ru_2(S_2CNMe_2)_5]Cl$	$CDCl_3$	3.05, 3.24, 3.53, 3.56, 3.68	1 530	
β-$[Ru_2(S_2CNMe_2)_5]Cl$	$CDCl_3$	3.22(2), 3.56, 3.59, 3.595	1 540	
$[Ru_2(S_2CNMe_2)_5]$			1 520	1 525
$[Ru(S_2CNMe_2)_3]$			1 519	1 523
β-$[Ru_2(S_2CNEt_2)_5][BF_4]$	$CDCl_3$	CH_3: 1.07, 1.42 CH_2: 3.58, 3.94 [d]	1 510 1 527 (sh)	
β-$[Ru_2(S_2CNEt_2)_5]Cl$	$CDCl_3$	CH_3: 1.07, 1.42 CH_2: 3.61, 3.95	1 513	
$[Ru(S_2CNEt_2)_3]$			1 490	

[a] Chemical shift relative to $SiMe_4$ (δ = 0 p.p.m.); integrated peak areas are unity unless noted in parentheses. [b] Absorptions due to $[BF_4]^-$ at 1 060br, 529, and 539 cm⁻¹. [c] Absorptions due to $[PF_6]^-$ at 845 and 568 cm⁻¹. [d] Resonances appeared as complex multiplets.



α-$[Ru_2(S_2CNMe_2)_5]^+$

(I)

The ion α-$[Ru_2(S_2CNMe_2)_5]^+$ is converted into β-$[Ru_2(S_2CNMe_2)_5]^+$ on heating in $CHCl_3$ solution (Cl^-, $[BF_4]^-$, or $[PF_6]^-$ salts). This interconversion was monitored qualitatively by ^1H n.m.r. spectroscopy and quantitatively by spectrophotometric means on $[Ru_2(S_2CNMe_2)_5]Cl$. Monitoring at 450 nm, the α isomer was readily converted into the β isomer at 60 °C in $CHCl_3$ with a first-order rate constant, *k*, of *ca.* 1 × 10^{-4} s⁻¹.

The ^1H n.m.r. properties of the complexes are of particular interest (Table 4). Both isomers showed five methyl singlets which are derived from the non-rotation

---

* *Note added at proof:* A detailed description of the crystal structure of β-$[Ru_2(S_2CNEt_2)_5][BF_4]$ has now appeared (B. M. Mattson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, 1976, **15**, 564). Some electrochemical data are reported for $[Ru(S_2CNR_2)_3]$ and the β forms (presumably?) of $[Ru_2(S_2CNR_2)_5][BF_4]$.

[21] R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Austral. J. Chem.*, 1973, **26**, 2533.

[22] A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, 1974, **13**, 1933.

[23] A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, 1975, **14**, 2980.

[24] D. Taylor, unpublished work.

about the C · · · N bond and the resulting diastereotopic nature of these groups. The chemical-shift values of these resonances are particularly dependent on the solvent and the counter anion. Interestingly, heating of β-$[Ru_2(S_2CNMe_2)_5][BF_4]$ in $(CD_3)_2SO$ to 120 °C did not cause the general five-line spectrum to coalesce, although two resonances did overlap, presumably due to a fortuitous temperature dependence of their chemical-shift values, suggesting that the C · · · N bond is quite resistant to rotation.

With both isomers, $[Eu(fmod)_3]$ (fmod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate) induced the shifts illustrated in Figure 1 in the ^1H n.m.r. spectra. The association equilibrium between the complexes of Ru^{III} and Eu^{III} was rather slowly established, especially for β-$[Ru_2(S_2CNMe_2)_5]^+$ which required many hours to equilibrate. Equilibrium was not achieved for the data shown. This fact presumably accounts for the non-linear dependence of chemical shift on the concentration of $[Eu(fmod)_3]$. As no splitting of the five-line spectrum in the presence of $[Eu(fmod)_3]$ was observed, for either the α or β isomer, it is reasonable to assume that lanthanoid attachment occurs at the S groups along the C_2 axis of the dimers. The methyl groups may be assigned assuming that those groups closest to the paramagnetic Eu^{III} are shifted most.[25]

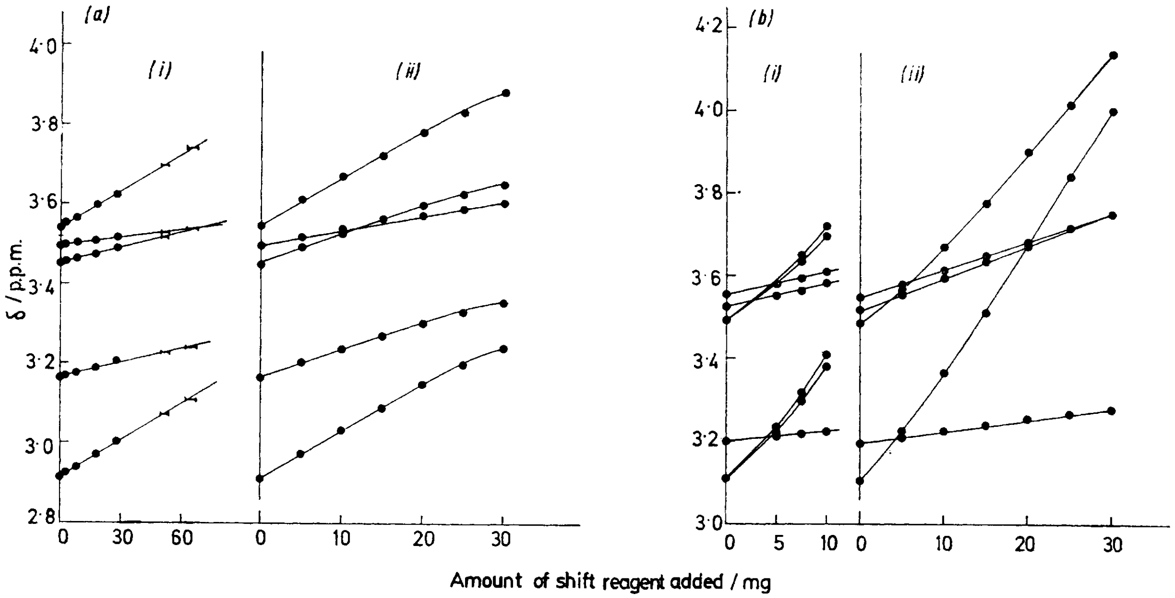


FIGURE 1 Chemical shifts of CH_3 resonances of (*a*) α- and (*b*) β-$[Ru_2(S_2CNMe_2)_5][BF_4]$ in CD_2Cl_2 on addition of the shift reagents (*i*) $[Eu(fmod)_3]$ and (*ii*) OPTISHIFT. Horizontal bars on (*i*) do not represent additional additions but refer to the 30-mg addition solution which was allowed to progress further toward equilibrium

Addition of the optically active shift reagent OPTISHIFT, tris[3-(heptafluoropropylhydroxymethylene)-D-camphorato]europium(III), to β-$[Ru_2(S_2CNMe_2)_5]^+$ resulted in the same overall trends in shifting the resonances as observed with $[Eu(fmod)_3]$ although the two peaks most sensitive to shift reagent were each split into two peaks of equal area (Figure 1). Both ruthenium(III) centres are of the same chirality and hence the observed splitting requires that the complex in solution is an equimolar mixture of the diruthenium complexes, each pair being of opposite chirality. The *X*-ray crystallographic results also show that the crystal contains equal numbers of dimers of opposite chirality,[24] *i.e.* ΔΔ and ΛΛ.

Although the α-$[Ru_2(S_2CNMe_2)_5]^+$ dimer contains two ruthenium(III) centres of opposite chirality, the crystals consist of equal numbers of dimeric cations with the combinations of ΔΛ and ΛΔ (*X*-ray crystallography).[24] However, on interaction with OPTISHIFT, no splitting of peaks was observed (Figure 1) suggesting that the α complexes are not sufficiently sensitive to the chiral environment or that the ^1H n.m.r. shifts are accidentally coincident for these species.

Redox Properties of $[Ru_2(S_2CNMe_2)_5]^+$.—Both the diruthenium(III) species are electroactive and behave similarly with the added feature that the two ruthenium(III) ions comprising the dimer are reduced at different potentials (Table 5). Hence following the first reduction (5) the resulting complex is formally a mixed-valence

$$[Ru_2(S_2CNMe_2)_5]^+ + e^- \rightleftharpoons [Ru_2(S_2CNMe_2)_5] \quad (5)$$

complex of Ru^{II} and Ru^{III}. Interestingly, α-$[Ru_2(S_2CNMe_2)_5]^+$ is slightly easier (by 35 mV) to reduce than β-$[Ru_2(S_2CNMe_2)_5]^+$, a trend which becomes more pronounced for the second reduction step (6) where the reduction potentials for the two isomers differ by 105 mV.

$$[Ru_2(S_2CNMe_2)_5] + e^- \rightleftharpoons [Ru_2(S_2CNMe_2)_5]^- \quad (6)$$

Furthermore, the reduction of β-$[Ru_2(S_2CNMe_2)_5]$ to the anion results in a rapid conversion of this isomer (*i.e.* β-$[Ru_2(S_2CNMe_2)_5]^-$) into the α anion. The reduction product of α-$[Ru_2(S_2CNMe_2)_5]$ does not isomerise. These

---

[25] J. Reuben, *Progr. N.M.R. Spectroscopy*, 1973, **9**, 1.

factors are illustrated by the cyclic voltammograms in Figure 2. When this information is coupled with the fact (see earlier) that the more stable cationic isomer is the β form, the relative orders of stability can be determined. The equilibrium position for α-$[Ru_2(S_2CNMe_2)_5]$ and β-$[Ru_2(S_2CNMe_2)_5]$ has been determined in CH_2Cl_2 solution saturated with $[NEt_4][ClO_4]$ at 20 °C. Solutions obtained from the electrolytic reduction of separate solutions of α- and β-$[Ru_2(S_2CNMe_2)_5]^+$ were allowed to equilibrate and the concentration of each isomeric form was monitored by a.c. voltammetry of the $[Ru_2(S_2CNMe_2)_5]$–$[Ru_2(S_2CNMe_2)_5]^-$ couples. Ratios of a.c. peak currents at equilibrium suggested $K(\beta^0/\alpha^0) = [\beta\text{-}Ru_2(S_2CNMe_2)_5]/[\alpha\text{-}Ru_2(S_2CNMe_2)_5] = 5.6$. From the addi-

TABLE 5

Redox properties of diruthenium complexes

	A.c. voltammetry [b]			Cyclic voltammetry [c]		
Couple ($[BF_4]^-$ salts) [a]	E_p/V	$\Delta E_{\frac{1}{2}}$/mV	i_p/c / mA dm^3 mol^{-1}	i_p^f/i_p^r	ΔE_p/mV	$i_p/cv^{\frac{1}{2}}$ / mA s$^{\frac{1}{2}}$ dm^3 mol^{-1} mV$^{-\frac{1}{2}}$
α-$[Ru_2(S_2CNMe_2)_5]^{+/0}$ [d]	−0.273	101	80	0.9	76	5.3
β-$[Ru_2(S_2CNMe_2)_5]^{+/0}$ [d]	−0.308	99	80	1.0	71	6.0
α-$[Ru_2(S_2CNMe_2)_5]^{0/-}$	−0.721	97	73	*e*	68	
β-$[Ru_2(S_2CNMe_2)_5]^{0/-}$	−0.826	97	59	*e*	76	
β-$[Ru_2(S_2CNMe_2)_5]^{+/0}$	−0.350	97	68	0.9	72	5.2
β-$[Ru_2(S_2CNEt_2)_5]^{0/-}$ [f]	−0.937	90	50	*e*	72	
α-$[Ru_2(S_2CNEt_2)_5]^{0/-}$ [f,g]	−0.818					
β-$[Ru_2\{S_2CN(CH_2Ph)_2\}_5]^{+/0}$	−0.175	122	53	1.0	86	4.3
β-$[Ru_2\{S_2CN(CH_2Ph)_2\}_5]^{0/-}$ [f]	−0.756	*h*	*h*	*h*	*h*	
α-$[Ru_2\{S_2CN(CH_2Ph)_2\}_5]^{0/-}$ [f,g]	−0.665					

[a] The superscript +/0 denotes the couple between positively charged and neutral species. [b] Peak to peak a.c. potential, 10 mV. [c] All data at scan rate of 200 mV s^{-1}. [d] Exhibited an irreversible oxidation at +1.27 V. [e] The ratio is scan-rate and temperature dependent (see text). [f] Assigned by analogy with the methyl derivatives. [g] Generated at electrode by isomerisation of β-$[Ru_2(S_2CNR_2)_5]^-$. [h] Conversion of the β to the α isomer was too rapid to afford meaningful data.

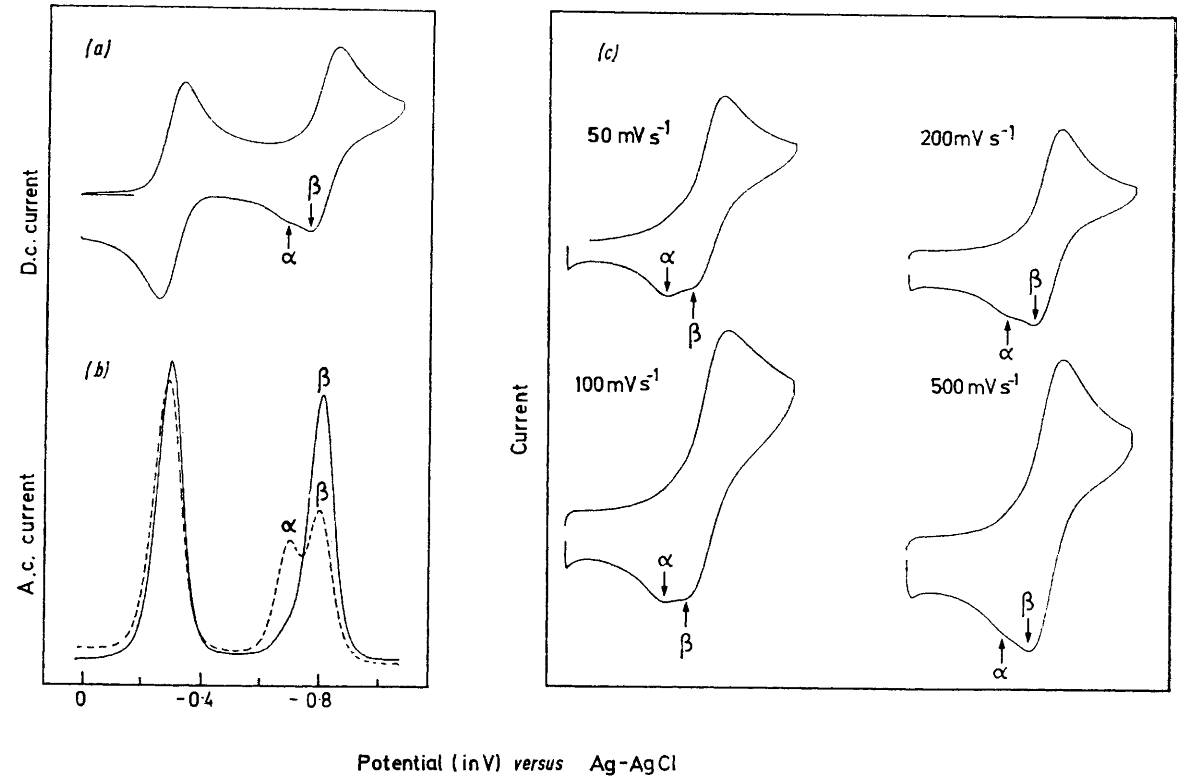


FIGURE 2 (*a*) Cyclic voltammogram of β-$[Ru_2(S_2CNMe_2)_5][BF_4]$ in acetone (0.1 mol dm^{-3} $[NEt_4][ClO_4]$). Zero current marked at the commencement of the voltammogram (scan rate 200 mV s^{-1}). (*b*) Cyclic a.c. voltammogram [solution as in (*a*)]: (——), cathodic scan; (— — —), anodic scan obtained by holding at cathodic limit for *ca.* 10 s. Scan rate 100 mV s^{-1}. In both (*a*) and (*b*) the second reduction process displays the $\beta^- \longrightarrow \alpha^-$ isomerisation of the anion. (*c*) Effect of scan rate on the $\beta^- \longrightarrow \alpha^-$ isomerisation of $[Ru_2(S_2CNMe_2)_5]^-$. Complex added to acetone (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) solution as β-$[Ru_2(S_2CNMe_2)_5]Cl$. Some recorder distortion was introduced at the scan rate of 500 mV s^{-1}. Redox processes centred at *ca.* −0.75 V tional redox data, the expressions (7) and (8) can be written.

$$K(\beta^+/\alpha^+) = K(\beta^0/\alpha^0)\exp\left\{\frac{nF}{RT}[E(\alpha^{0/+}) - E(\beta^{0/+})]\right\} = 22 \quad (7)$$

$$K(\beta^-/\alpha^-) = K(\beta^0/\alpha^0)\exp\left\{\frac{nF}{RT}[E(\beta^{0/-}) - E(\alpha^{0/-})]\right\} = 0.09 \quad (8)$$

The stability order of the two isomers, as a function of ruthenium oxidation state, is dependent on the electronic and steric requirements of the d^5 ruthenium(III) and d^6 ruthenium(II) ions. The proximity of the ruthenium(III) ions in the $t_2{}^5$–$t_2{}^5$ cation (2.787 Å) favours the unique bridging-ligand structure. The absence of Ru–Ru bonding in the $t_2{}^6$–$t_2{}^6$ anion is associated with a Ru–Ru distance which is too large to favour this type of bridging ligand {*e.g.* the Rh–Rh distance [17] in the isoelectronic complex $[Rh_2(S_2CNMe_2)_5]^+$ is 3.556 Å}.

It is also worth noting the difference in the rates of the isomerisation reactions (9) and (10) where the Ru–Ru

$$\beta\text{-}[Ru_2(S_2CNMe_2)_5]^- \longrightarrow \alpha\text{-}[Ru_2(S_2CNMe_2)_5]^- \quad (9)$$

$$\alpha\text{-}[Ru_2(S_2CNMe_2)_5]^+ \longrightarrow \beta\text{-}[Ru_2(S_2CNMe_2)_5]^+ \quad (10)$$

bonded cation isomerises rather slowly at 60 °C whilst the anionic species isomerises quickly, even at room temperature. The rate of conversion of β-$[Ru_2(S_2CNMe_2)_5]^-$ into α-$[Ru_2(S_2CNMe_2)_5]^-$ was estimated from the cyclic voltammograms of the $[Ru_2(S_2CNMe_2)_5]$–$[Ru_2(S_2CNMe_2)_5]^-$ couple [Figure 2(*c*)] using the working curve of Nicholson and Shain [26] for the follow-up reaction to the electron-transfer step. For this purpose the $\beta^- \longrightarrow \alpha^-$ conversion was considered to be irreversible. Approximate k values of 0.04, 0.06, 0.16, 0.38, 0.50, and 1.48 s^{-1}, obtained at 5, 15, 25, 35, 45, and 55 °C, were used in a plot of log k against $1/T$ to obtain a projected value at 60 °C of $k = 2 \pm 1$ s^{-1} for the isomerisation. This approach helps minimise the errors caused by non-reproducible surface effects at the platinum electrode.

This marked effect in isomerisation rates of at least a factor of 10^4 probably reflects the influence of the Ru–Ru bond on the energetics of rotation at the ruthenium centres, although the requirement of the breaking of a Ru–S bond to allow these isomerisations may also be more difficult with the cationic species. The difficulty of breaking the Ru–Ru bond in $[Ru_2(S_2CNMe_2)_5]^+$ is shown when a mixture of the two isomers was heated under reflux in MeOH for 5 h with $[S_2CNMe_2]^-$ in an attempt to cleave the dimer into two molecules of $[Ru(S_2CNMe_2)_3]$. Thin-layer chromatography showed that very little $[Ru(S_2CNMe_2)_3]$ was formed. This behaviour contrasts with that observed [16] with α-$[Co_2(S_2CNR_2)_5]^+$ which is readily cleaved with anionic and neutral chelates (L) to form $[Co(S_2CNR_2)_3]$, $[Co(S_2CNR_2)_2L]$, and $[Co(S_2CNR_2)_2L]^+$. These observations help substantiate the proposed [17] intramolecular mechanism for interconversion of isomers of the α and β types.

The new neutral dimer, $[Ru_2(S_2CNMe_2)_5]$, was isolated by two routes, both of which utilise the lower solubility of the neutral complex in acetone and methanol compared with the cationic precursor $[Ru_2(S_2CNMe_2)_5]^+$ as $[BF_4]^-$ and Cl^- salts, respectively. Tetrahydridoborate reduction of the cation readily afforded a pure sample of the complex, although the neutral species was also isolated from electrolysis studies. The spectral properties of the new complex are included in Tables 2 and 4. The problem of formulating $[Ru_2(S_2CNMe_2)_5]$ in terms of two delocalised $Ru^{2.5+}$ or as a mixed $Ru^{3+}Ru^{2+}$ species has not been examined and is worthy of further study.

We thank Drs. A. H. White and C. Raston for providing many of the $[Ru(S_2CNR_2)_3]$ complexes used in the electrochemical studies, and Dr. D. Taylor for the crystallographic studies.

[5/2552 *Received*, 31*st December*, 1975]

---

[26] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.