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Two New Ruthenium(II) Complexes involving Two Different Chelation Modes of Partially Chlorinated 2-(Benzylthio)azobenzene

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Abstract. Complex A, [RuCl($C_{19}H_{16}N_2S$)($C_{19}H_{14.75}Cl_{0.25}N_2S$)], mean $M_r = 752.9$, triclinic, $P\bar{1}$, $a = 16.116\,(3)$, $b = 10.519\,(8)$, $c = 10.416\,(4)$ Å, $\alpha = 74.91\,(4)$, $\beta = 95.19\,(2)$, $\gamma = 83.44\,(3)°$, $V = 1680.4$ Å^3, $Z = 2$, $D_x = 1.49$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 6.87$ cm^{-1}, $T = 295$ K, $F(000) = 768.0$, $R = 0.051$ for 3966 [$I > 2\sigma(I)$] reflections. Complex B, [Ru($C_{19}H_{15}N_2S$)($C_{19}H_{14.70}Cl_{0.30}N_2S$)], mean $M_r = 718.2$, triclinic, $P\bar{1}$, $a = 9.831\,(3)$, $b = 10.217\,(2)$, $c = 16.349\,(5)$ Å, $\alpha = 78.81\,(2)$, $\beta = 77.43\,(3)$, $\gamma = 88.23\,(2)°$, $V = 1572.2$ Å^3, $Z = 2$, $D_x = 1.52$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 6.47$ cm^{-1}, $T = 295$ K, $F(000) = 733.6$, $R = 0.061$ for 2901 [$I > 2\sigma(I)$] reflections. The metal coordination spheres are complex A RuClCN$_2$S$_2$ (N,N and S,S pairs are *cis–cis*); and complex B RuC$_2$N$_2$S$_2$ (N,N and S,S pairs *trans–cis*). Both coordination spheres are distorted octahedral. The Ru—C bond exerts a dominant *trans* effect. The N=N distances [1.272 (8)–1.300 (10) Å] suggest the presence of substantial Ru–azo π back bonding.

Introduction. Structural studies on ruthenium complexes of azo ligands have been sparse. The available data have revealed the presence of interesting features such as strong π back bonding (Seal & Ray, 1984) and unusual hydrogen bonding (Chakravarty, Chakravorty,

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Cotton, Falvello, Ghosh & Lisbona, 1983). Herein we report the structures of two complexes – blue-violet (A) and red-violet (B) – afforded by the reaction of the title ligand (I) with ruthenium trichloride in boiling methanol and separated by chromatography on silica gel. In complex A, [RuCl(C$_{19}$H$_{16}$N$_2$S)(C$_{19}$H$_{15}$N$_2$S)], one ligand is N,S bonded (II) and the other is tridentate through C,N,S (III) via ortho-metallation. In complex B, [Ru(C$_{19}$H$_{15}$N$_2$S)$_2$] both ligands are tridentate (III).

(I)   (II)   (III)
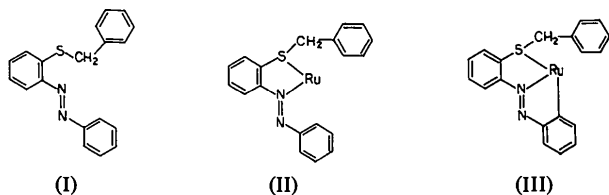
Experimental. Complex A: crystals from dichloromethane–heptane (1/4); complex B: from dichloromethane–acetonitrile (1/5); specimens 0·15 × 0·20 × 0·28 mm (complex A) and 0·33 × 0·35 × 0·20 mm (complex B). Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo Kα radiation; cell parameters from 25 randomly chosen reflections to $\theta = 15·6°$ for complex A [$\theta = 19·4°$ for complex B]; $2° \leq \theta \leq 25°$, ω–2θ scan; $h0$ to 19 [0 to 11], k–12 to 12 [−11 to 11], l −12 to 12 [−18 to 18], 6138 [5879] unique reflections measured, 2172 [2978] unobserved with $I \leq 2\sigma(I)$. Intensity variation of standards in both cases <4%; no absorption correction. Atomic scattering factors, f' and f'' for Ru from International Tables for X-ray Crystallography (1974). Structures solved by Patterson and Fourier methods. Difference Fourier map computed after isotropic refinement on F in each case ($R = 0·09$, 0·10 for A, B) showed an extra peak near C(15). Heights of extra peak in weighted Fourier maps (Sim, 1960) were 3·0 and 5·0 e Å^{-3} respectively compared with 3·0 to 6·5 e Å^{-3} for C atoms. This was subsequently found to be Cl with occupancy 0·254 (8) in A and 0·298 (10) in B, obtained by refining occupancy factor with the other parameters. In last stages of refinement weighting scheme, $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ calculated (Seal & Ray, 1981); for A: $|F_o| \leq 14·90$, $\sigma(F) = 0·238F_o$; $14·90 < |F_o| \leq 17·06$, $\sigma(F) = 0·183F_o$; $17·06 < |F_o| \leq 19·16$, $\sigma(F) = 0·119F_o$; $19·16 < |F_o| \leq 23·00$, $\sigma(F) = 0·085F_o$; $23·00 < |F_o| \leq 26·53$, $\sigma(F) = 0·070F_o$; $26·53 < |F_o| \leq 30·58$, $\sigma(F) = 0·059F_o$; $30·58 < |F_o| \leq 36·14$, $\sigma(F) = 0·050F_o$; $|F_o| > 36·14$, $\sigma(F) = 0·040F_o$; for B: $|F_o| < 17·70$, $\sigma(F_o) = 0·180F_o$; $17·70 < |F_o| \leq 23·50$, $\sigma(F_o) = 0·100F_o$; $23·50 < |F_o| \leq 29·20$, $\sigma(F_o) = 0·088F_o$; $29·20 < |F_o| \leq 38·00$, $\sigma(F_o) = 0·067F_o$; $|F_o| > 38·00$, $\sigma(F_o) = 0·060F_o$. In both cases positional and anisotropic thermal parameters of all non-hydrogen atoms and occupancy of Cl atom attached to C(15)

refined by block-diagonal least squares; H atoms in calculated positions, coordinates and thermal parameters fixed. For complex A, refinement converged at $R = 0·051$, $wR = 0·056$, $S = 0·830$ for 3966 reflections, max. $\Delta/\sigma = 0·836$, max., min. peaks in final difference map +0·6, −0·5 e Å^{-3} respectively. Refinement of complex B converged at $R = 0·061$, $wR = 0·075$, $S = 1·155$ for 2901 reflections, max. $\Delta/\sigma = 0·601$, max., min. peaks in final difference map +0·9, −1·1 e Å^{-3} around Ru atom, generally <0·5 e Å^{-3} elsewhere. All computations on a Burroughs B6700 computer with programs EXFFT and SEARCH of MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), XRAY ARC (Vickery, Bright & Mallinson, 1971), PARST (Nardelli, 1982).

Discussion. Final atomic parameters and selected bond distances and angles are in Tables 1* and 2 respectively. ORTEP (Johnson, 1965) views of the asymmetric units of complexes A and B are shown in Figs. 1 and 2. The complexes consist of discrete monomeric units. The metal coordination spheres are: A RuClCN$_2$S$_2$ and B RuC$_2$N$_2$S$_2$ – both distorted octahedral. The chelate bite angles range from 76·2 (5) to 84·9 (1)°; the C, N bite angles being particularly acute (Table 2). Each chelate ring is planar with no atom deviating by more than 0·15 Å; the corresponding chelate rings in the two halves of each complex are approximately orthogonal to each other, the dihedral angles lying in the range 86·3 (1) to 92·9 (3)°.

In complex A the N,N and S,S coordinating pairs have cis–cis geometry while in B they are trans–cis (Table 2). From covalent radii values, the Ru–C(sp^2) single-bond distance is estimated to be 2·06 Å, but observed values span the relatively wide range 1·96– 2·16 Å (Clark, Waters & Whittle, 1975; Jameson, Muster, Robinson, Wingfield & Ibers, 1981; McGuiggan & Pignolet, 1982). The Ru–C distances in A and B fall well within this range. In A the Ru–S bond trans to Ru–N is 2·323 (2) Å while that trans to Ru–C is 2·436 (2) Å. In B both Ru–S bonds are trans to Ru–C bonds with lengths of 2·407 (2) and 2·437 (2) Å. A dominant trans effect of the Ru–C bond is thus revealed. The Ru–N distances in A and B are close to those previously reported in Ru–azo complexes (Seal & Ray, 1984; Chakravarty et al., 1983). The N=N distances, ranging from 1·272 (8) to 1·30 (1) Å, are relatively long, reflecting the presence of substantial π back bonding in the Ru–azo fragment (Seal & Ray, 1984) of both complexes.

Table 1. *Refined parameters for non-hydrogen atoms*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}		x	y	z	B_{eq}
Complex A					**Complex B**				
Ru	0.24016 (3)	0.13208 (5)	0.06411 (5)	2.79	Ru	0.76075 (8)	0.17622 (7)	0.22176 (4)	2.26
Cl(1)	0.2364 (1)	0.2676 (2)	0.2178 (2)	4.06	S(1)	0.5629 (2)	0.1901 (2)	0.3360 (1)	2.58
S(1)	0.0943 (1)	0.0966 (2)	0.0811 (2)	4.03	S(2)	0.7718 (2)	0.4158 (2)	0.1665 (1)	2.91
S(2)	0.2934 (1)	−0.0394 (2)	0.2544 (2)	3.74	N(1)	0.8650 (7)	0.1485 (7)	0.3150 (5)	2.52
N(1)	0.1885 (3)	0.2998 (4)	−0.0721 (4)	3.34	N(2)	0.9973 (8)	0.1254 (7)	0.3033 (5)	3.01
N(2)	0.2335 (4)	0.3872 (5)	−0.1269 (5)	3.99	N(3)	0.6757 (8)	0.1751 (7)	0.1213 (4)	2.91
N(3)	0.2575 (5)	−0.0075 (5)	−0.0340 (5)	3.33	N(4)	0.6241 (9)	0.0675 (7)	0.1080 (5)	3.26
N(4)	0.2672 (4)	−0.0014 (6)	−0.1552 (6)	5.46	C(1)	0.375 (1)	0.4922 (9)	0.4420 (6)	3.15
C(1)	0.0793 (6)	−0.1492 (9)	0.325 (1)	6.69	C(2)	0.260 (1)	0.515 (1)	0.5037 (7)	4.42
C(2)	0.1130 (8)	−0.265 (1)	0.425 (1)	8.85	C(3)	0.151 (1)	0.422 (1)	0.5337 (7)	4.67
C(3)	0.1548 (8)	−0.259 (1)	0.541 (1)	9.34	C(4)	0.161 (1)	0.305 (1)	0.5028 (8)	5.16
C(4)	0.1646 (9)	−0.137 (1)	0.560 (1)	10.04	C(5)	0.272 (1)	0.283 (1)	0.4402 (7)	4.17
C(5)	0.1334 (7)	−0.022 (1)	0.4639 (9)	7.88	C(6)	0.3816 (9)	0.3759 (9)	0.4095 (6)	2.92
C(6)	0.0898 (5)	−0.0269 (8)	0.3449 (8)	5.44	C(7)	0.502 (1)	0.3603 (9)	0.3375 (6)	3.45
C(7)	0.0558 (5)	0.0999 (8)	0.2417 (8)	5.83	C(8)	0.6536 (9)	0.1609 (8)	0.4215 (5)	2.65
C(8)	0.0494 (4)	0.2572 (7)	−0.0226 (6)	4.16	C(9)	0.580 (1)	0.1489 (9)	0.5064 (5)	3.09
C(9)	−0.0389 (5)	0.2976 (8)	−0.0395 (8)	5.71	C(10)	0.654 (1)	0.1205 (9)	0.5709 (6)	4.06
C(10)	−0.0722 (5)	0.4212 (9)	−0.1220 (9)	6.72	C(11)	0.796 (1)	0.102 (1)	0.5524 (6)	4.37
C(11)	−0.0213 (5)	0.5034 (8)	−0.1928 (8)	6.35	C(12)	0.867 (1)	0.1121 (9)	0.4689 (6)	3.72
C(12)	0.0635 (5)	0.4653 (7)	−0.1789 (7)	5.21	C(13)	0.793 (1)	0.1432 (8)	0.4034 (5)	2.67
C(13)	0.0999 (4)	0.3423 (6)	−0.0923 (6)	3.97	C(14)	1.049 (1)	0.1243 (8)	0.2167 (5)	2.86
C(14)	0.3180 (4)	0.3361 (6)	−0.0968 (6)	3.77	C(15)	1.193 (1)	0.1047 (9)	0.1908 (7)	4.38
C(15)	0.3754 (5)	0.4139 (7)	−0.1608 (8)	5.35	C(16)	1.246 (1)	0.098 (1)	0.1048 (7)	5.10
C(16)	0.4591 (5)	0.3606 (8)	−0.1400 (8)	5.86	C(17)	1.156 (1)	0.111 (1)	0.0493 (7)	4.51
C(17)	0.4846 (5)	0.2337 (8)	−0.0578 (8)	5.54	C(18)	1.016 (1)	0.133 (1)	0.0758 (6)	3.81
C(18)	0.4272 (4)	0.1578 (7)	0.0069 (6)	4.43	C(19)	0.9558 (9)	0.1432 (8)	0.1622 (5)	2.85
C(19)	0.3417 (4)	0.2084 (6)	−0.0073 (6)	3.23	C(20)	1.074 (1)	0.484 (1)	0.2402 (6)	4.28
C(20)	0.4863 (5)	−0.2467 (8)	0.4724 (8)	6.36	C(21)	1.134 (1)	0.548 (1)	0.2872 (7)	5.82
C(21)	0.5141 (6)	−0.322 (1)	0.6050 (9)	8.09	C(22)	1.131 (1)	0.683 (1)	0.2753 (8)	6.13
C(22)	0.4854 (6)	−0.2845 (9)	0.7104 (8)	6.95	C(23)	1.066 (2)	0.757 (1)	0.216 (1)	6.52
C(23)	0.4292 (6)	−0.1734 (9)	0.6884 (8)	6.52	C(24)	1.001 (1)	0.692 (1)	0.1683 (7)	4.66
C(24)	0.4014 (5)	−0.0953 (8)	0.5589 (8)	5.70	C(25)	1.006 (1)	0.5526 (9)	0.1780 (5)	3.08
C(25)	0.4321 (4)	−0.1316 (7)	0.4516 (6)	4.43	C(26)	0.952 (1)	0.484 (1)	0.1190 (6)	4.21
C(26)	0.4055 (5)	−0.0430 (7)	0.3105 (7)	4.75	C(27)	0.7164 (9)	0.4104 (9)	0.0714 (5)	2.86
C(27)	0.2940 (4)	−0.1754 (6)	0.1837 (6)	3.75	C(28)	0.708 (1)	0.5269 (9)	0.0104 (7)	3.94
C(28)	0.3087 (4)	−0.3060 (6)	0.2635 (7)	4.67	C(29)	0.668 (1)	0.521 (1)	−0.0635 (6)	4.26
C(29)	0.3051 (5)	−0.4087 (7)	0.2046 (9)	5.53	C(30)	0.631 (1)	0.400 (1)	−0.0780 (6)	4.24
C(30)	0.2867 (5)	−0.3818 (7)	0.0669 (9)	5.88	C(31)	0.631 (1)	0.285 (1)	−0.0178 (6)	3.56
C(31)	0.2699 (5)	−0.2505 (7)	−0.0128 (7)	4.77	C(32)	0.673 (1)	0.2903 (9)	0.0566 (5)	2.94
C(32)	0.2743 (4)	−0.1466 (6)	0.0453 (6)	3.72	C(33)	0.6402 (9)	−0.0392 (8)	0.1730 (6)	2.74
C(33)	0.2410 (5)	0.1214 (7)	−0.2544 (6)	4.89	C(34)	0.584 (1)	−0.165 (1)	0.1712 (7)	4.46
C(34)	0.1568 (6)	0.1685 (8)	−0.2897 (7)	6.13	C(35)	0.595 (1)	−0.270 (1)	0.2343 (7)	4.23
C(35)	0.1313 (6)	0.2792 (9)	−0.4023 (8)	7.11	C(36)	0.667 (1)	−0.253 (1)	0.2966 (6)	4.28
C(36)	0.1912 (7)	0.3386 (9)	−0.4723 (8)	7.30	C(37)	0.719 (1)	−0.1295 (9)	0.2991 (6)	3.14
C(37)	0.2753 (7)	0.2893 (9)	−0.4341 (8)	7.17	C(38)	0.703 (1)	−0.0142 (8)	0.2363 (5)	2.70
C(38)	0.3013 (6)	0.1792 (8)	−0.3259 (7)	5.78	Cl†	1.3163 (7)	0.1114 (8)	0.2407 (4)	1.88
Cl*	0.3299 (7)	0.5573 (9)	−0.288 (1)	8.07					

* Attached to C(15); occupancy 0.254 (8).
† Attached to C(15); occupancy 0.298 (10).

Table 2. *Selected bond distances* (Å) *and angles* (°)

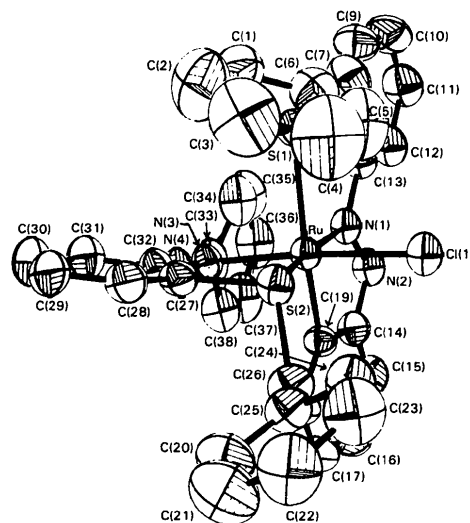|	Complex A	Complex B		Complex A	Complex B
Ru–S(1)	2.436 (2)	2.407 (2)	Ru–S(2)	2.323 (2)	2.437 (2)
Ru–N(1)	1.991 (4)	1.987 (8)	Ru–N(3)	2.005 (6)	2.000 (8)
Ru–C(19)	2.022 (6)	2.004 (9)	S(1)–C(7)	1.844 (9)	1.823 (9)
S(1)–C(8)	1.782 (6)	1.790 (10)	S(2)–C(26)	1.841 (7)	1.865 (10)
S(2)–C(27)	1.771 (7)	1.767 (10)	N(1)–C(13)	1.426 (8)	1.458 (10)
N(3)–C(32)	1.462 (7)	1.426 (10)	N(1)–N(2)	1.285 (7)	1.293 (10)
N(3)–N(4)	1.272 (8)	1.300 (11)	Ru–Cl(1)	2.405 (2)	
Ru–C(38)		2.000 (8)			
S(1)–Ru–S(2)	94.2 (1)	94.0 (1)	S(1)–Ru–N(1)	83.6 (2)	83.5 (2)
S(1)–Ru–N(3)	91.1 (2)	103.7 (3)	C(19)–Ru–S(2)	105.4 (2)	94.7 (3)
C(19)–Ru–N(1)	77.4 (2)	76.6 (3)	C(19)–Ru–N(3)	89.6 (2)	95.6 (3)
S(2)–Ru–N(3)	84.9 (2)	82.4 (2)	Ru–S(1)–C(8)	95.6 (3)	97.4 (3)
Ru–S(2)–C(27)	99.1 (2)	96.8 (3)	Ru–N(1)–C(13)	121.6 (4)	120.8 (6)
Ru–N(3)–C(32)	117.8 (4)	122.8 (6)	Ru–N(1)–N(2)	121.4 (4)	123.5 (6)
Ru–N(3)–N(4)	132.7 (5)	122.5 (6)	S(1)–Ru–Cl(1)	92.3 (1)	
C(19)–Ru–Cl(1)	90.8 (2)		Cl(1)–Ru–S(2)	84.1 (1)	
Cl(1)–Ru–N(1)	84.4 (2)		N(1)–Ru–N(3)	106.7 (2)	169.4 (3)
S(1)–Ru–C(38)		85.7 (3)	C(19)–Ru–C(38)		93.0 (4)
S(2)–Ru–N(1)	168.2 (2)	105.2 (2)	C(38)–Ru–N(1)		96.6 (3)
C(38)–Ru–N(3)		76.4 (3)			

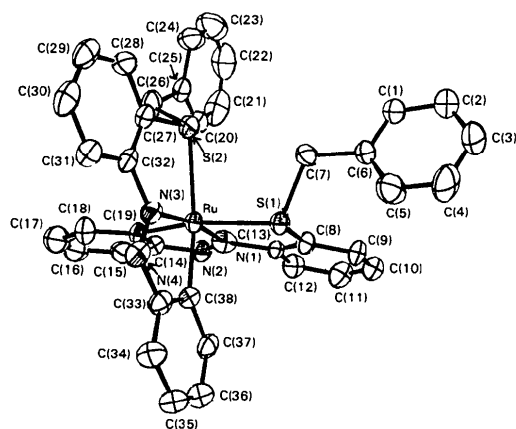Fig. 1. Atom-labelling scheme and 50% probability ellipsoids for complex A [C(8), C(18) not labelled].

Fig. 2. Atom-labelling scheme and 50% probability ellipsoids for complex *B*.

Regarding the partial presence of Cl attached to C(15) in *A* and *B*, we note that in the syntheses the source of the metal is ruthenium trichloride, which can conceivably act as a chlorinating agent like its congener ferric chloride (De La Mare & Ridd, 1959). However, the origin of the specificity of chlorine substitution at C(15) is unclear at present.

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Structure of Tetrameric η-Cyclopentadienyl Chromium Sulfide

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Abstract. Tetrakis(η-cyclopentadienyl)tetra-μ_3-thiotetrachromium(III), [Cr$_4$S$_4$(C$_5$H$_5$)$_4$], $M_r = 596.64$, $C2/c$, $a = 17.582$ (8), $b = 8.045$ (3), $c = 16.137$ (8) Å, $\beta = 116.5$ (4)°, $V = 2043$ (7) Å^3, $Z = 4$, $D_x = 1.939$ g cm^{-3}, Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 216$ cm^{-1}, $F(000) = 1200$, $T = 293$ K, $R = 5.1\%$, 1560 unique reflections. The cubane structure of the tetramer can be viewed as being formed from two interpenetrating tetrahedra of chromium and sulfur atoms with each chromium coordinated to three other chromium atoms, three sulfur atoms and one η^5-cyclopentadienyl ring. The bond lengths and angles of the cyclopentadienyl rings are normal.

Introduction. Transition-metal–sulfur cubane systems are of continuing interest on account of their biological

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