

Thio Derivatives of β -Diketones and their Metal Chelates. XX* Magnetic Moments of Some Ruthenium(III) Chelates of Fluorinated Monothio- β -diketones

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Abstract

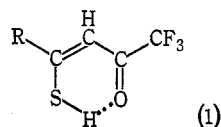
Magnetic data have been obtained for ruthenium(III) chelates of the fluorinated monothio- β -diketones $\text{RC}(\text{SH})=\text{CHCOCF}_3$ ($\text{R} = 2\text{-thienyl}, \beta\text{-naphthyl}, \text{Ph}, p\text{-MeC}_6\text{H}_4, m\text{-MeC}_6\text{H}_4, m\text{-ClC}_6\text{H}_4, m\text{-BrC}_6\text{H}_4$). The compounds are low-spin ($S = 1/2$) with moments in the range $1.68\text{--}1.84$ B.M. at room temperature; the moments decrease with decrease in temperature.

All ruthenium(III) complexes so far investigated are of the low-spin type with one unpaired electron (2T_2 state). Monomeric complexes have room-temperature magnetic moments in the range $1.65\text{--}2.24$ B.M.^{1,2} However, some dimeric complexes have been reported as having moments in the range $2.55\text{--}3.15$ B.M.¹ The ruthenium(III) complexes of the β -diketones, acetylacetone, benzoylacetone and dibenzoylmethane, have effective moments of $1.65\text{--}1.81$ B.M. at room temperature.² The dithioacetylacetonato complex $\text{Ru}(\text{CH}_3\text{CS}=\text{CHCSCH}_3)_3$ has a moment (μ_{eff}) of 1.72 B.M. at 290 K but the moment falls to 1.59 at 110 K. However, recalculation of the moment by means of equation (1)

$$\mu_{\text{corr}} = 2.84[\chi'_M(T-\theta)]^{1/2} \quad (1)$$

gives a temperature-independent moment (μ_{corr}) of 1.76 B.M.³ Since iron(III) complexes of monothio- β -diketones exhibit thermal equilibrium between high-spin ($S = 5/2$) and low-spin ($S = 1/2$) states,⁴ we have investigated the magnetic behaviour of ruthenium(III) complexes of some monothio- β -diketones.

The magnetic susceptibilities of the ruthenium(III) chelates of the fluorinated monothio- β -diketones (1; $\text{R} = 2\text{-thienyl}, \beta\text{-naphthyl}, \text{Ph}, p\text{-MeC}_6\text{H}_4, m\text{-MeC}_6\text{H}_4, m\text{-ClC}_6\text{H}_4, m\text{-BrC}_6\text{H}_4$) have been determined over the temperature range $83\text{--}293$ K and in three instances the susceptibility was measured at 373 K also. The room-



* Part XIX, *Aust. J. Chem.*, 1975, 28, 1249.

¹ Figgis, B. N., and Lewis, J., in 'Modern Coordination Chemistry' (Eds J. Lewis and R. G. Wilkins) pp. 448, 449 (Wiley-Interscience: New York 1960).

² Grobelny, R., Jezowska-Trzebiatowska, B., and Wojciechowski, W., *J. Inorg. Nucl. Chem.*, 1966, 28, 2715.

³ Heath, G. A., and Martin, R. L., *Aust. J. Chem.*, 1970, 23, 1721.

⁴ Ho, R. K. Y., and Livingstone, S. E., *Aust. J. Chem.*, 1968, 21, 1987.

temperature moments range from 1.68 to 1.84 B.M. and the compounds obey the Curie-Weiss law with large negative values for the Weiss constant θ (see Table 1).

Table 1. Magnetic moments of ruthenium chelates $\text{Ru}(\text{RCS}=\text{CHCOCF}_3)_3$ at 293 K

R	μ_{eff} (B.M.)	θ (K)	R	μ_{eff} (B.M.)	θ (K)
$\text{C}_4\text{H}_3\text{S}$	1.68	-12	<i>m</i> - MeC_6H_4	1.84	-47
$\beta\text{-C}_{10}\text{H}_7$	1.73	-30	<i>m</i> - ClC_6H_4	1.82	-57
Ph	1.75	-61	<i>m</i> - BrC_6H_4	1.77	-27
<i>p</i> - MeC_6H_4	1.78	-37			

Table 2. Magnetic data on ruthenium chelates $\text{Ru}(\text{RCS}=\text{CHCOCF}_3)_3$
 T in K; χ'_M in $\text{m}^3 \text{mol}^{-1}$; μ_{eff} and μ_{corr} in B.M.

R	T	$10^6 \chi'_M$	μ_{eff}	μ_{corr}	R	T	$10^6 \chi'_M$	μ_{eff}	μ_{corr}
$\text{C}_4\text{H}_3\text{S}$	293	1187	1.68	1.71	$\beta\text{-C}_{10}\text{H}_7$	373	999	1.73	1.80
	253	1369	1.67	1.71		333	1099	1.72	1.80
	213	1638	1.68	1.72		293	1270	1.73	1.82
	173	1984	1.66	1.72		233	1484	1.67	1.78
	133	2483	1.63	1.71		173	1926	1.64	1.78
Ph	83	3856	1.61	1.72	<i>p</i> - MeC_6H_4	83	3552	1.54	1.80
	293	1299	1.75	1.92		293	1347	1.78	1.89
	253	1486	1.74	1.93		253	1543	1.77	1.87
	213	1684	1.70	1.93		213	1775	1.75	1.89
	173	1954	1.65	1.92		173	2097	1.71	1.88
<i>m</i> - MeC_6H_4	133	2354	1.59	1.92	<i>m</i> - ClC_6H_4	133	2615	1.67	1.89
	83	3560	1.54	2.08		83	3669	1.57	1.88
	373	1145	1.86	1.97		373	1123	1.84	2.08
	323	1313	1.85	1.98		333	1238	1.82	1.96
	290	1454	1.84	1.99		293	1413	1.82	1.98
<i>m</i> - BrC_6H_4	223	1772	1.79	1.96		253	1568	1.79	1.96
	173	2194	1.75	1.97		203	1870	1.75	1.96
	123	2906	1.70	2.00		153	2306	1.69	1.95
	93	3599	1.64	2.02		103	3026	1.56	1.95
	333	1225	1.82	1.86					
	293	1444	1.85	1.90					
	243	1591	1.77	1.83					
	193	1944	1.74	1.82					
	143	2590	1.73	1.83					
	93	3711	1.67	1.82					

The magnetic data are given in Table 2; the moments (μ_{eff}) decrease appreciably with temperature. The corrected values, obtained by means of equation (1), are virtually temperature-independent and lie within the range 1.71–2.08 B.M. Large negative values of θ are characteristic of ruthenium(III) complexes of β -diketon² and the mono- and di-thio³ analogues. However, the use of equation (1) for these compounds is probably not justified. It can be used when magnetic exchange interaction is present or in certain other situations but in the presence of an orbitally degenerate ground state ($^2T_{2g}$ in this case), split by spin-orbit coupling, equation (1) has little meaning and the significance of the Weiss constant θ is not clear.

Heath and Martin³ commented on the low moment of the dithioacetylacetone complex of ruthenium(III) at room temperature, since in the absence of axial distortion or extensive electron delocalization the room-temperature moments of ruthenium(III) complexes are predicted to be *c.* 2.1 B.M.⁵ The monothio- β -diketone complexes similarly have moments (μ_{eff}) below 2.1 B.M. at room temperature.

The magnetic moments of complexes with $^2T_{2g}$ ground terms are expected to decrease with decreasing temperature because of the progressive quenching of the orbital angular momentum by spin-orbit coupling which removes the degeneracy of the triplet ground term.³ Axial distortion from O_h symmetry—which is appreciable in complexes of monothio- β -diketones—further quenches the orbital contribution and brings the moment closer to the spin-only value. It has been suggested⁶ that extensive spin-orbit coupling can reduce the moment below the spin-only value of 1.73 B.M. Consequently, it must be accepted that for these ruthenium(III) complexes the magnetic moment is a function of temperature.

Experimental

Ruthenium Complexes

The preparations of the ruthenium complexes of (1; R = C_4H_9S , β - $C_{10}H_7$, Ph, *p*- MeC_6H_4) have been⁷ or will be⁸ described. The other complexes were prepared as follows. Ruthenium trichloride trihydrate (1.0 g; 3.8 mmol) in alcohol (50 ml) was added to a solution of the monothio- β -diketone (11.4 mmol) in alcohol (50 ml). The mixture was heated at the reflux for 4 h and filtered hot. The filtrate, upon standing in the refrigerator overnight, deposited black crystals of the ruthenium complex. The crystals were filtered off, and washed with a little ice-cold alcohol; yield 15–25%.

Tris[4-(3'-bromophenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-onato]ruthenium(III), m.p. 212° (Found: C, 34.8; H, 1.7; S, 8.9. $C_{30}H_{15}Br_3F_9O_3RuS_3$ requires C, 34.9; H, 1.5; S, 9.3%).

Tris[4-(3'-chlorophenyl)-1,1,1-trifluoro-4-mercaptobut-3-en-2-onato]ruthenium(III), m.p. 218° (Found: C, 40.0; H, 1.7; S, 10.2. $C_{30}H_{15}Cl_3F_9O_3RuS_3$ requires C, 40.0; H, 1.7; S, 10.7%).

Tris[1,1,1-trifluoro-4-mercapto-4-(3'-methylphenyl)but-3-en-2-onato]ruthenium(III), m.p. 183° (Found: C, 47.4; H, 3.0. $C_{33}H_{24}F_9O_3RuS_3$ requires C, 47.4; H, 2.9%).

Magnetic Susceptibility Measurements

The magnetic susceptibilities of the complexes were measured in an atmosphere of nitrogen on a Newport variable-temperature Gouy balance.

Manuscript received 7 July 1975

⁵ Figgis, B. N., 'Introduction to Ligand Fields' p. 248 *et seq.* (Wiley-Interscience: New York 1966).

⁶ Figgis, B. N., *Trans. Faraday Soc.*, 1961, **57**, 198.

⁷ Das, M., and Livingstone, S. E., *Aust. J. Chem.*, 1974, **27**, 2115.

⁸ Livingstone, S. E., and Moore, D. S., unpublished data.